Life cycle assessment of the production of xanthate salts and of their application for ARD mitigation

Makhosazane Chucky Kunene

November 2014

Dissertation in fulfilment of
MASTERS IN CHEMICAL ENGINEERING
In the Department of Chemical Engineering
UNIVERSITY OF CAPE TOWN

This work is based on research supported by Senmin® International and the South African Research Chairs Initiative of the Department of Science and Technology and National Research Foundation of South Africa (NRF). Any opinion, finding, conclusion or recommendation expressed in this material is that of the author and the NRF does not accept any liability in this regard.

Dedication

To the Kunene family: My late father, Lancelot Kunene, my mother, Theresa Kunene and my five sisters, Gugu, Nomcebo, Sithembile, Xolile and Mbali.

Synopsis

Xanthate salts are commonly used as collectors in the mineral processing of sulphide ores. In more recent studies, xanthate has also been used in the environmental desulphurisation flotation of sulphidic mine tailings and coal waste, with a view to mitigating acid rock drainage (ARD) risks through the pre-disposal removal of sulphide minerals. In South Africa, xanthate salts are produced by Senmin® International (Pty Ltd) via the conversion of carbon disulphide at its facility in Sasolburg. In 2010, Senmin® commissioned a new state-of-the-art plant for the production of carbon disulphide using methane rather than charcoal as a carbon source. Although this process has many advantages over the old process, no attempt has been made to date to quantify the environmental benefits. Similarly, whilst the technical feasibility of using xanthate salts in the desulphurisation flotation to reduce the ARD-generating potential of mine tailings has been demonstrated in a number of case studies, little attention has been given to the broader environmental implications of this tailings treatment option. The life cycle assessment (LCA) approach proves to be a valuable tool to study the environmental aspects and potential impacts throughout the life cycle of a product or process. In this study, LCA was used as a tool to assess the implications of the new carbon disulphide production process on the environmental performance of subsequent xanthate salt production, as well as the environmental consequences of using these salts in the downstream desulphurisation of base metal sulphide tailings.

The objectives of the study were achieved by conducting two inter-related LCA studies: LCA of xanthate production (LCA 1) and LCA of ARD mitigation (LCA 2). These LCA studies followed the protocol set out in the ISO 14040 standards using the Simapro software package (version 7.3.3). The first LCA study was a cradle-to-gate comparison of current and previous carbon disulphide production processes for the production of xanthate. Data was collected in two ways: the foreground data was sourced at the plant in Sasolburg, whilst ecoinvent database was used for background data for the production of 1 tonne of carbon disulphide. To quantify the identified environmental impacts, namely climate change, terrestrial acidification, human toxicity, freshwater ecotoxicity and fossil depletion, ReCiPe, a midpoint life cycle impact assessment (LCIA) method was chosen. Study results confirmed that the new carbon disulphide production facility has a significantly lower environmental footprint than the old charcoal-based process, based on the studied environmental impacts. This improvement reflected positively on the environmental performance of the subsequent xanthate production process. It was also established that further environmental improvement in the recovery and reuse of generated steam in the new carbon disulphide process can significantly lower the environmental impacts of xanthate production.

The second LCA study examined the environmental consequences of incorporating a desulphurisation flotation process unit for pre-disposal removal of sulphur from base metal sulphide waste streams by developing two scenarios. The first scenario entailed treatment of a tailings slurry stream using a conventional method (termed the base case scenario). The second treatment scenario (referred to as the desulphurisation flotation scenario), entailed the tailings slurry being subjected to desulphurisation flotation, using a xanthate collector. Data based on literature information, in-house knowledge, the ecoinvent database and the first LCA study, was used to generate model parameters at a reference flow rate of 100 tonnes of dry tailings per day for both scenarios. Two LCIA impact assessment methodologies were used to evaluate and compare the potential environmental impacts of the two tailings treatment scenarios for seven key midpoint impact categories. Human and ecotoxicity impacts were assessed using USEtox, while climate change, fossil fuel depletion, terrestrial acidification, natural land transformation and urban land occupation, used the ReCiPe method. Finally, a sensitivity analysis was conducted to determine the sensitivity of selected impact categories to key parameters, namely electricity consumption, ore mineralogy, mobilisation of metals as well as xanthate deportment to the tailings storage facility.

In accordance with the LCA study conducted here, the downstream application of xanthate in the desulphurisation flotation of a base metal sulphide tailings sample results in a significant decrease in human toxicity, ecotoxicity, urban land occupation and natural land transformation impacts, but an increase in climate change, fossil fuel depletion and terrestrial acidification impacts. Desulphurisation flotation also offers the opportunity for improved recovery of valuable resources, such as water, residual metals and sulphur. Detailed assessment would, however, require the need to expand the studied system boundary to capture the environmental benefits of upstream and downstream utilisation of the recovered resources. Sensitivity analysis results showed that varying the relevant parameters (electricity, ore mineralogy and mobilisation of metals) can greatly affect the environmental performance of the compared scenarios. This, therefore, motivates the need to improve the quality of input data to describe the system, particularly pertaining to electricity consumption, mobility of tailings components during disposal, and the deportment and behaviour of xanthate. Despite the benefits of LCA as a tool for evaluating the life cycle impacts of a process or product, the study also indicated that the state-of-the-art LCA tools are still deficient in terms of their ability to adequately assess the environmental impacts associated with solid mineral wastes. This pertains, in particular, to aqueous acidification, salinisation and trace metal impact, which are characterised by high uncertainty factors. Recommendations have been made to develop life cycle indicators which extend and compliment current LCIA methods such as USEtox and ReCiPe, with a view to address these limitations. It is also recommended that a water impact assessment study be conducted

according to the recently published ISO 14064 standards, as the methods for water use in LCA were still undergoing improvement when the study started.

Despite limitations with respect to current LCA modelling tools and available parameters, this study provides useful information in the identification of opportunities for improving environmental performance across the carbon disulphide-xanthate-desulphurisation flotation process system, thus playing a key role in guiding further developmental studies.

Acknowledgements

My heartfelt thanks go to my supervisors: Dr. Jenny Broadhurst for her guidance, encouragement and knowledge throughout this study; Professor Harro von Blottnitz for his motivation and advice on Life Cycle Assessment (LCA); Dr. Patrick Dicks for his interest and insightful comments.

Sincere appreciation also goes to the following people:

- Professor J-P. Franzidis for granting me the opportunity and support of the project through the Minerals to Metals Research Initiative.
- The Acid Rock Drainage (ARD) and Environmental and Process Systems Engineering (E&PSE) discussion groups for the valuable comments and discussions given during the course of the project.
- Mr.Wilhelm Havenga and the staff at Senmin®, for their assistance when collecting all the required data for this study, insightful comments and making my stay comfortable in Sasolburg during the plant visit.
- Thabi and Wale for your friendship, support and assistance with SimaPro software.
- To all friends and colleagues in the Chemical Engineering Department who assisted in this project in one way or the other. To the Holy Name Catholic Church and the Sri Chinmoy Meditation Centre in Observatory for the spiritual enrichment during my stay in Cape Town. The Pfaff family for the love and lovely meals you shared during my write-up stage. To my family, nieces and nephews for their love, support and encouragement throughout this study. I am truly blessed beyond measure to have you in my life.

To the Highest Supreme, my gratitude-filled heart bows down to Thee.

Table of Contents

List of Figures

List of Tables

Glossary

List of abbreviations and nomenclature used in this work

ABA	Acid base accounting
AMD	Acid mine drainage
ANC	Acid neutralising capacity
ARD	Acid rock drainage
ATSDR	Agency for Toxic Substances and Disease Registry
CO_2	Carbon dioxide
CS_2	Carbon disulphide
CTUe	Comparative Toxic Units (ecotoxicity)
CTUh	Comparative Toxic Units (human toxicity)
EIA	Environmental Impact Assessment
EPA	Environmental Protection Agency
ICP-MS	Inductively coupled plasma-mass spectrometry – Element analysis technique
ISO	International Standards Organisation
KWh	Kilowatt hour
LCA	Life cycle assessment
LCI	Life cycle inventory
LCIA	Life cycle impact assessment
LC_{50}	Median lethal concentration
LD_{50}	Median lethal dosage
MJ	Mega joules
MPA	Maximum potential acidity
NAPP	Net acid production potential
NEM	National Environmental Management

NICNAS	National Industrial Chemicals Notification & Assessment Scheme
NOHSC	National Occupational Health and Safety Commission
OSHA	Occupational Safety and Health Administration
PEC	Priority Existing Chemical
ppm	Parts per million
RA	Risk Assessments
SETAC	Society of environmental toxicity and chemistry
SEX	Sodium ethyl xanthate
SO_2	Sulphur dioxide
UNEP	United Nations Environmental Program
WHO	World Health Organisation
1,4-DB	1,4 Dichlorobenzene

Chapter 1

INTRODUCTION

A number of chemical manufacturing companies have for some time now attempted to ensure that their products are developed and used in a manner consistent with sustainability principles (Feng et al., 2010). This means taking into consideration multiple objectives and criteria, including the consumption of raw materials and energy, chemical toxicity risks and the production of pollutants and wastes. The mining industry is also keenly aware of its environmental performance, and is responding by taking measures to assess and control those activities that affect the environment (Reid et al., 2007). One of the major environmental issues facing the mining industry is acid mine drainage (AMD), also referred to as acid rock drainage (ARD), which occurs when sulphide minerals are exposed to water and oxygen. ARD not only reduces the pH of surface and ground waters, but also results in elevated salt and metal concentrations. One of the prevention strategies proposed to mitigate this problem involves application of a technique known as desulphurisation flotation. This process targets the pre-disposal removal of ARD generating sulphide minerals, producing a large volume of sulphide-lean tailings which are non-acid forming, and a smaller volume of sulphide-rich concentrate.

It is in this context that the environmental performance of xanthate production and its application in the mitigation of ARD are investigated. Life cycle assessment (LCA) is a potentially suitable tool in this regard as it emphasises the product stewardship dimensions of products over their entire life cycle. In this study, life cycle assessment (LCA) tools are used to identify and compare environmental impacts associated with process routes for xanthate salts production, and the downstream application of these salts in so far as they apply to the mitigation of ARD.

1.1 Background

1.1.1 Xanthate production from CS_2 at Senmin®

Xanthate is an organosulphur compound with the formula $ROCS_2^-M^+$ (R = alkyl; M+ = Na^+, K^+). Most xanthate salts are yellow in colour and are commonly used in the mining industry as collectors in the flotation of sulphide minerals, metallic elements (e.g., copper, nickel, silver, gold) and some oxidised minerals of lead and copper, from ore slurries. Examples of

xanthate salts commonly used as sulphide collectors are sodium and potassium ethyl xanthate, potassium amyl xanthate and sodium isopropyl and isobutyl xanthate. This use was first introduced by Keller in 1927 (Keller, 1927).

Xanthate salts are produced by Senmin® International (Pty, Ltd) at their production facility in Sasolburg, South Africa. Sasolburg is a chemical city in the Free State province, named after the South African-innovated petroleum-from-oil company, Sasol. Despite the major occupation of the petrochemical industry in the area, it also houses other large companies including Karbochem (manufacturer of various types of synthetic rubber), Omnia Fertiliser (producer of fertilisers) as well as Senmin®. Senmin®, a company owned by African Explosives and Chemical Industries (AECI), is a manufacturer and supplier of a range of chemicals used in the beneficiation of minerals since 1967. Most of its products are utilised in the froth flotation and tailings treatment segments of the mining industry in South Africa, Southern Africa and further afield. In addition, the company also provides customers with value-adding expertise in the handling and dosage of its products. Xanthate salts are one of their major products.

In order to manufacture this product, a separate plant is required that produces carbon disulphide (CS_2), which is a major reactant in the production of xanthate collectors. Carbon disulphide is converted to xanthate salts through reaction with an alcohol and sodium or potassium hydroxide (Equation 1).

$$ROH + CS_2 + NaOH \rightarrow ROCS_2Na + H_2O \qquad \text{Equation 1}$$

(Where R is an alkyl group)

Prior to 2010, carbon disulphide (CS_2) was produced in a batch process by heating charcoal to 750-900 ^{o}C in the presence of vaporised low-ash sulphur (Equation 2)

$$C + S_2 \rightarrow CS_2 \qquad \text{Equation 2}$$

Since 2010, however, a new state-of-the-art plant has been commissioned. This plant involves the catalytic reaction of methane (natural gas) and sulphur vapour (Equation 3), and subsequent recovery of sulphur from the H_2S gas produced (Equation 4).

$$CH_4 + 4S^0 \rightarrow CS_2 + 2H_2S \qquad \text{Equation 3}$$

$$2H_2S + O_2 \rightarrow 2S^0 + 2H_2O_{\text{(steam)}} \qquad \text{Equation 4}$$

The new process offers many advantages over the previous process. In particular, it utilises a readily available source of carbon and operates at lower temperatures. Due to faster reaction rates and higher conversions, the process can be designed for higher capacities of production.

The steam generated can also be utilised further, thus improving overall energy efficiency. However, the environmental benefits of this major shift from charcoal to methane as a source of carbon disulphide production have not been rigorously quantified to date.

1.1.2 Xanthate use in the mining industry

Acid rock drainage (ARD) is a phenomenon that occurs when reactive sulphide minerals are exposed to water and oxygen, resulting in acidic pH values and elevated concentrations of dissolved salts and metals. Various authors (Hesketh, 2010a; Napier-Munn et al., 2008; Cilliers, 2006) have indicated the need to provide a long-term solution to ARD pollution risks associated with sulphide-bearing mine wastes. Environmental desulphurisation flotation is a pollution prevention technique which involves the pre-disposal removal of sulphide from mine wastes (Kazadi Mbamba, 2011; Harrison et al., 2010; Hesketh, 2010a; Bois et al., 2005; Benzaazoua and Kongolo, 2003; Benzaazoua et al., 2000). In recent studies at the University of Cape Town, South Africa, xanthate salts have been used in the desulphurisation flotation of copper sulphide tailings (Harrison et al., 2010; Hesketh et al., 2010c) and coal wastes (Kazadi Mbamba, 2011; Harrison et al., 2010). Similar studies have also been conducted in Canada, where the use of xanthate salts as a collector has been shown to be effective in the desulphurisation flotation of base metal and gold tailings (Bois et al., 2005; Benzaazoua and Kongolo, 2003; Benzaazoua et al., 2000).

These studies have shown that the removal of sulphide minerals from sulphide-bearing tailings prior to disposal can effectively remove the long-term risks of ARD, whilst simultaneously providing opportunities for additional value recovery. The environmental impacts of desulphurised tailings have been analysed, where metal deportment and mobility were evaluated. Desulphurisation flotation resulted in a substantial decrease in the soluble metal concentration (Hesketh, 2010a). However, just like conventional beneficiation processes rely mostly on organic reagents (collectors, frothers and additives) for the extraction of metals, desulphurisation flotation also depends on these reagents. Yet, in the case of xanthate collectors, it must be acknowledged that its production involves a highly toxic intermediate (CS_2) and that this chemical may also be formed again when the xanthates degrade in the environment (NICNAS, 1995; Xu et al, 1988). Previous studies have also not taken cognisance of the indirect environmental impacts associated with the additional consumption of energy and raw materials.

1.1.3 Life cycle assessment (LCA)

A range of environmental assessment tools for chemicals exists. Risk assessments (RA) tools are suitable for site-specific purposes. Environmental impact assessment (EIA) is prescribed

when a new production or storage facility is planned. For product stewardship purposes, life cycle assessment (LCA) is a suitable tool (Hauschild and Alting, 1998). Life cycle assessment (LCA) is a potentially suitable tool to assess the production, use and disposal of xanthate salts, as it has been specifically developed to assess the potential environmental impacts and resources used throughout a product's lifecycle from cradle to grave, i.e. from raw material acquisition, production, downstream use and final disposal (ISO 14040, 2006).

The purpose of using this tool varies from one application to another and each application may require a different level of data quality in terms of accuracy and reliability. It can be directly used for product development and improvement, strategic planning, public policy making and marketing (ISO 14040, 2006). In product development it is used as an environmentally conscious process design tool with a view to identifying and addressing environmental impacts at an early stage of the design process, while in product improvement it is used to analyse an already made product or process and mostly focuses on the materials and the resources that affect the product significantly. This enables several products, processes or services to be compared with respect to each other from an environmental point of view. Chemical products (e.g. carbon disulphide) can be well analysed using a so-called 'cradle-to-factory gate' approach, i.e. from raw material acquisition to the production stage of the product, and the data collected can be used as generic data in the full LCA of the final product (e.g. xanthate) (Klopffer, 2005). This approach can also be used to study the comparative advantages or disadvantages of different production routes and/or raw materials used for producing the same chemical (Klopffer, 2005).

Life cycle assessment is designed to detect the shifting of environmental burdens, which it achieves by (i) extending the assessment upstream and downstream of the production phase, which typically is the focus of other assessment approaches, and (ii) by considering a range of different environmental impacts (including resource depletion, climate forcing, habitat changing mechanisms such as eutrophication, as well as human and environmental toxicity).Whilst some of the impacts assessed in an LCA are easily derived from the quantified resource uses and environmental releases, assessment methods for other impacts, especially those relating to toxicity, have proven to be much harder to develop for reliable use (Finnveden et al., 2009).

1.2 Problem statement

Despite the apparent benefits, to date no attempt has been made to rigorously and quantitatively assess the environmental consequences of the new (methane-based) carbon disulphide process for xanthate production route at the Sasolburg facility.

Similarly, studies of the environmental performance and consequences of the downstream desulphurisation flotation process for ARD mitigation have been limited to date.

1.3 Project scope

This study uses the life cycle assessment (LCA) approach to identify and compare the environmental impacts of the current and previous carbon disulphide production processes, as well as the subsequent effects of such on xanthate production and its down-stream application, insofar as it pertains to the desulphurisation of base metal sulphide tailings. Furthermore, this information will be used to identify opportunities for improving environmental performance across the carbon disulphide-xanthate-ARD mitigation process system, thereby playing a key role in guiding further developmental studies and in assisting both the producers and users of xanthate chemicals in meeting their commitments to sustainable development.

The study was largely desk-based and involved the application of life cycle assessment tools and techniques to model and link three sub-systems in the xanthate life cycle: (i) the production of CS_2 (ii) the production of xanthate salts from CS_2 (iii) the use of xanthate in the desulphurisation process. The main methodological steps involved in this study are:

(i) Development of flow sheets and inventory databases.
(ii) LCA modelling using the commercially available SimaPro software, and the ReCiPe and USEtox impact assessment methods.
(iii) Interpretation and analysis of model output data, in terms of sensitivity to key model inputs, availability and quality of input data and capabilities of current LCA models.

This investigation is in partial fulfilment of the research component of a Master's Degree programme in Chemical Engineering at the University of Cape Town, and is in line with Senmin®'s commitment to optimising the environmental performance of their operations and maximising product stewardship.

1.4 Dissertation structure

Chapter 1 introduces the project and includes background information, the problem statement and project scope. Chapter 2 reviews the relevant literature and draws up the project objectives and key research questions, whilst Chapter 3 summarises the methodology. Chapters 4 and 5 summarise and discuss the results of the life cycle assessment studies of the xanthate production and downstream ARD mitigation processes respectively. Finally,

Chapter 6 concludes the study and makes recommendations for further work. This structure is outlined in Figure 1.

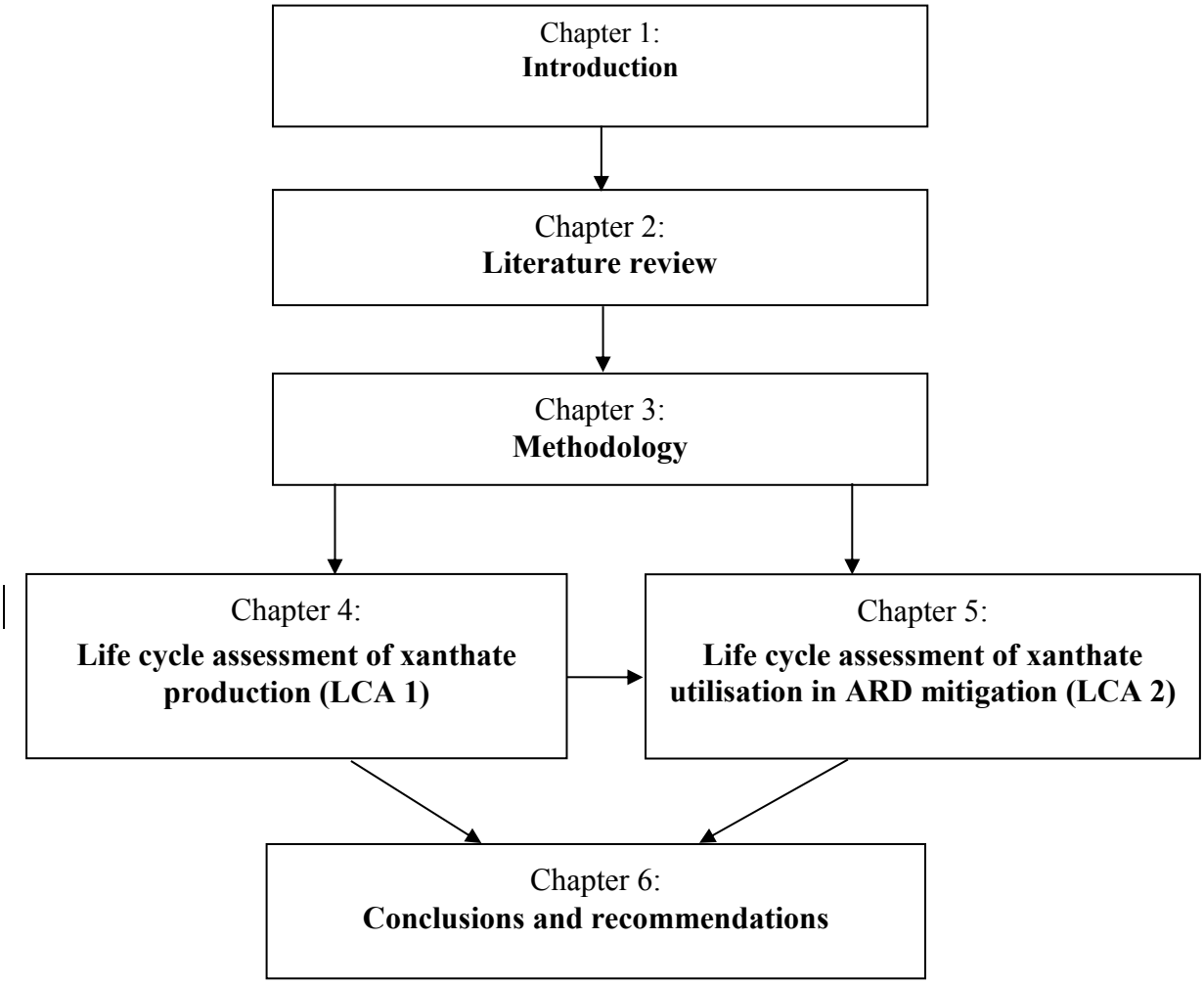


Figure 1: Schematic outline of the dissertation structure

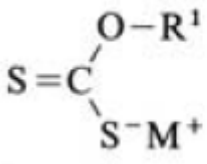
Chapter 2

LITERATURE REVIEW

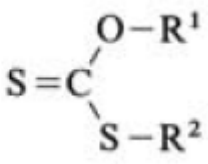
This chapter provides a detailed review and assessment of the relevant literature pertaining to xanthate production, its use in ARD mitigation and a LCA review. Sections 2.1 and 2.2 describe xanthate and carbon disulphide respectively, with particular emphasis on their production, environmental impacts and toxicity. Section 2.3 provides information about acid rock drainage from mine waste and the use of xanthate in the desulphurisation flotation process for mitigation of ARD risk. In Sections 2.4 and 2.5, the LCA tool is defined in terms of its framework, methodologies, applications and limitations. Finally, the main findings from the literature review are summarised (Section 2.6) and research objectives developed (Section 2.7).

2.1 Xanthate Description

Xanthate is an organosulphur compound. The term refers to both salts and esters of xanthic acid with the structures shown below. Note: R = alkyl; M+ = Na^+, K^+



Xanthate salts



Xanthate esters

The name xanthate is derived from the Greek word ‘xanthos’, which means yellow. It was introduced by Zeise, (1822), who discovered this class of compounds that is defined by a number of different terms including xanthogenates, carbondithioates, dithiocarbonates, and sodium or potassium salts of xanthic (or dithiocarbonic) acid. Xanthates salts vary in colour from yellow to cream, and are soluble in water. The primary use for xanthate salts of the alkali metal group is as a collector in the flotation of metallic sulphides ores. They are also used as vulcanising agents in the manufacture of rubber, as herbicides, insecticides, fungicides, high pressure lubricant additives, analytical procedures (trace analysis of metal ions and alcohols by high performance liquid chromatography) and as intermediates in the manufacture of viscose/rayon and cellophane.

2.1.1 Xanthate production and properties

Xanthate salts are prepared by reacting sodium or potassium hydroxide with an alcohol and carbon disulphide. As an example, Equation 5 shows the reaction of sodium hydroxide with carbon disulphide and ethanol to form sodium ethyl xanthate and water:

$$CH_3CH_2OH + CS_2 + NaOH \rightarrow CH_3CH_2OCS_2Na + H_2O \qquad \text{Equation 5}$$

The production process is essentially a batch type, closed process and is carried out in steel reactors. The reaction temperature is generally kept below $40^{O}C$, since the decomposition of xanthate increases with temperature. Cooling is necessary to minimise side reactions. There are four types of xanthates (ethyl, butyl, propyl and amyl) that are generally produced in various combinations with sodium and potassium, which are stabilisers in the chemical formula. For example, some of the commercially used xanthates salts include:

- sodium ethyl xanthate (SEX), $C_2H_5OCSSNa$
- potassium ethyl xanthate (PEX), $C_3H_5KOS_2$
- sodium isopropyl xanthate (SIPX), $C_4H_7NaOS_2$
- sodium isobutyl xanthate (SIBX), $C_5H_{10}OS_2Na$
- potassium amyl xanthate (PAX), $C_5H_{11}OCSSK$

These salts are generally produced in dry forms, such as powder, granules, pellets, tablets or flakes, usually at 85- 95% purity, or in liquid form at 40% purity. At the production process of sodium ethyl xanthate (SEX) at Coogee Chemical plant in Australia, sodium ethyl xanthate is produced in liquid form (40-50% purity) from ethanol, aqueous sodium hydroxide and carbon disulphide (Figure 2). This process is also similar to the production at Senmin® in South Africa (explained at length in Chapter 4 of the thesis).

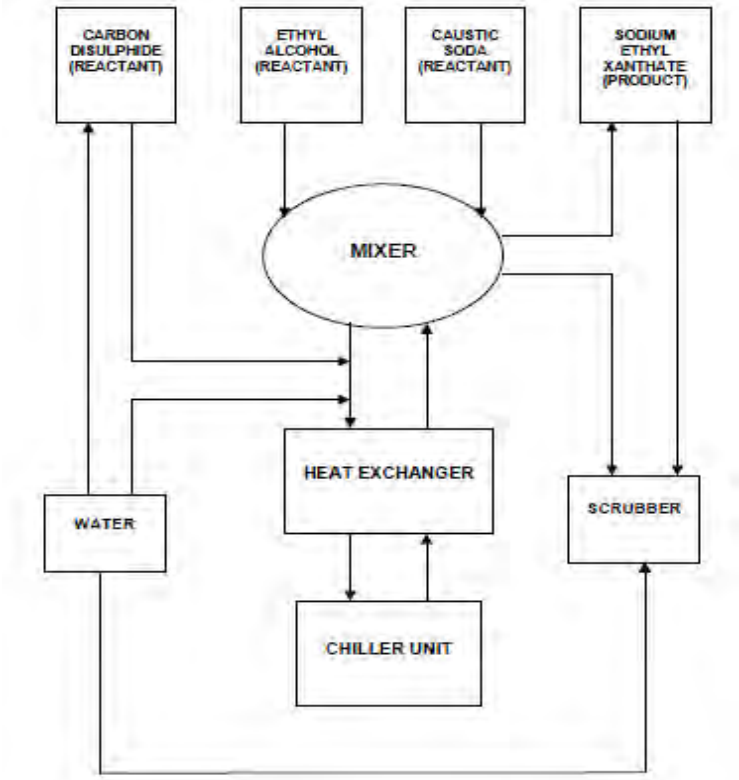


Figure 2: Process flow diagram for sodium ethyl xanthate manufacture at Coogee Chemicals (NICNAS, 2000)

Currently, SNF Flomin own and operate one of the largest production plants of xanthate chemicals in the world at their facility in Qingdao, China. By the year 1980, it was estimated that a total of 52 000 tonnes of xanthates was consumed annually by the mining industry worldwide (Harris, 2000). Most of the mining industry across the globe uses xanthate. The Australian mining industry has been using xanthates for over 35 years, and in the year 2000, up to 10 000 tonnes of sodium ethyl xanthate were produced and about 6,000 tonnes were imported mostly from China (NICNAS, 2000).

Xanthates are unstable compounds and decompose in the presence of water. The rate of xanthate decomposition increases as the xanthate concentration increases (for example 25% relative to 10% solution of sodium ethyl xanthate), the pH decreases below pH 7, and the temperature increases above 20^{o}C. In aqueous solution, xanthate salts can undergo a number of reaction mechanisms: (NICNAS, 1995).

A: Dissociation into alkali metal hydroxide and xanthic acid (reaction 6), which decomposes further into carbon disulphide and alcohol (reaction 7)

$$C_2H_5OCS_2M + H_2O \rightarrow C_2H_5OCS_2H + MOH \qquad \text{Equation 6}$$

$$C_2H_5OCS_2H \rightarrow CS_2 + C_2H_5OH \qquad \text{Equation 7}$$

B: Oxidation to dixanthogen (reaction 8)

$$2C_2H_5OCS_2M + H_2O + 1/2O_2 \rightarrow (C_2H_5OCS_2)_2 + 2MOH \quad \text{Equation 8}$$

C: Hydrolytic decomposition of xanthates which produce carbonate salts, carbon disulphide, trithiocarbonate salts and alcohol, that catalyses the reaction (reaction 9). Further hydrolysis may occur, with; trithiocarbonate being converted to carbonate salts and hydrogen sulphide (reaction 10), and carbon disulphide converting to carbon dioxide and hydrogen sulphide (reaction 11). Some of the carbon disulphide formed may evaporate and some may build up in the xanthate solution.

$$6C_2H_5OCS_2M + 3H_2O \rightarrow 6C_2H_5OH + M_2CO_3 + 3CS_2 + 2M_2CS_3 \quad \text{Equation 9}$$

$$M_2CS_3 + 3H_2O \rightarrow M_2CO_3 + 3H_2S \quad \text{Equation 10}$$

$$CS_2 + 2H_2O \rightarrow CO_2 + 2H_2S \quad \text{Equation 11}$$

(Where M is an alkali metal)

Mechanism A (reactions 6 and 7) and B (reaction 8) occur in acidic conditions, which are often associated with pore waters in sulphidic tailings deposits in the medium-long term. Mechanism C (reactions 9, 10 and 11) proceeds under neutral or alkaline conditions, such as those that occur during the sulphide ore flotation process (NICNAS, 1995).

However, in a recent study by Rostad et al. (2010), decomposition products reported by NICNAS (1995) were not detected in process waters discharged from a lead-zinc mine and mill or the tailings pond; only trace amounts of other xanthate degradation products (isopropyl xanthyl thiosulfonate and isopropyl xanthyl sulfonate) were detected (Rostad at al., 2010).

2.1.2 Xanthate environmental impacts and toxicity

Xanthate salts may pose a risk of adverse health and environmental effects during manufacturing, transportation and final disposal (NICNAS, 1995; NICNAS, 2000). Sodium ethyl xanthate is listed in the National Occupational Health and Safety Commission (NOHSC) List of Designated Hazardous Substances (NOHSC, 1999) as a ‘harmful’ substance when in contact with skin, eyes and swallowed. In Australia, sodium ethyl xanthate was declared a priority existing chemical (PEC) due to its high use in the mining industry, its potential for occupational and environmental exposure, and the lack of information regarding xanthate toxicity to humans, animals and natural ecosystems.

Prior to its declaration, a number of incidents involving exposure of humans to xanthate had been reported. These included an incident where 100 people were evacuated after a chemical leakage at a railway station. In another incident, bulker bags of xanthate catching fire in a mining site resulted in four people, including a fireman, being hospitalised due to inhalation of fumes. In another case, residents located at a nearby mine using xanthate complained of "headache, dizziness, nausea and foul odour" (NICNAS, 1995). Other symptoms of xanthate exposure included eye irritation, sore throat and impaired breathing. The Canadian Centre for Occupational Health and Safety (CCOHS) reported on an incident of a worker who opened a tank containing sodium ethyl xanthate (Moore, 1994). The worker lost consciousness and, on revival, he was restless, vomited, had difficulty in breathing and had teary eyes. In another case report (Donoghue, 1998), a worker was exposed to xanthate powder and solution during the mixing process. His skin turned green and he developed gastrointestinal symptoms the following day that lasted for three days. Urine samples measured two days after exposure had traces of a metabolite of CS_2 (<4 mg/l).

The main health hazard of xanthate to animals is oral and dermal acute toxicity (Roy, 2000). It is especially toxic to aquatic life and therefore its disposal is strictly controlled (NICNAS, 1995). Table 1 provides a summary of animal toxicological data (NICNAS, 1995). The organs in the studied species most affected are the central nervous system, liver and kidneys.

Table 1: An overall assessment of animal toxicological data (NICNAS, 1995)

Toxicological endpoint	Chemical	Species	Results	Target Organs
Acute oral	Sodium ethyl xanthate (10% solution)	Mice (male)	LD_{50} 730 mg/kg	Central nervous system, liver and spleen
	Other xanthates	Mice Rats	LD_{50} 411-583 mg/kg LD_{50} 1000-2000 mg/kg	Central nervous system, liver and kidneys
Acute dermal irritation/toxicity	Sodium ethyl xanthate			
	- 10% solution - 1mg/kg as paste	Rabbits Rabbits	Non-irritant LD_{50} < 1000 mg/kg	Liver, lungs, kidneys
Acute eye irritation	Sodium ethyl xanthate			
	- 10% solution - 30 mg powder	Rabbits Rabbits	Non-irritant Marked irritation immediately, moderate irritation up to 4 hours, mild irritation at 24 hrs	No gross pathology
Repeated dose toxicity				
- 4-month oral	Potassium butyl xanthate (10mg/kg)	Rats	Changes in the central nervous system, liver and spleen	Central nervous system, liver and kidneys
- 30-day inhalation	Potassium amyl xanthate			
	- 100 mg/m^3	Dogs Rabbits Rats Mice	Hepatotoxic effects No adverse effects No adverse effects Higher liver/body weight ratio	Liver - - Liver
	- 800 mg/m^3	Dogs Rabbits Rats Mice	Hepatotoxic effects No adverse effects Nephrotoxic effects 15/16 died, 5/15 showed hyperactivity and convulsions prior to death	Liver - Liver and kidneys Central nervous system and liver

Toxicity of xanthates to plants was investigated using Lemna minor (duckweed). Xu et al., (1988) found that sodium isobutyl, potassium and sodium isopropyl xanthate significantly affected leaf and root production in duckweed at 10 mg/l concentration and caused 100% lethality at exposure to concentration levels above 5 mg/l after three days. The authors concluded that these compound salts can be classified as harmful micro pollutants in aquatic systems at concentrations above 2 mg/l (Xu et al., 1988).

In terms of toxicity to fish, a study by Webb et al. (1976) investigated the toxicity of several flotation reagents on rainbow trout. He found that sodium ethyl and potassium amyl xanthate were the most toxic out of eight xanthate collectors used in a short-term test based on a LC_{50} in the range of 30-50 mg/l. However, long-term tests using flow-through bioassays resulted in higher toxicities than the short-term test. The toxicity of sodium ethyl xanthate towards rainbow trout was also analysed by Hawley (1977). He found that a concentration of 56 ppm killed all fish within four days under static conditions, and within eight days at a concentration of 1 ppm under flow-through conditions.

In addition to direct toxic effects, xanthate salts have also been found to enhance the bioavailability and uptake of toxic heavy metals such as cadium and mercury by fish and other organisms (Borg et al., 1988; Gottofrey et al., 1988; Block and Part, 1986). This is due to the ability to form complexes with toxic metals, thus enhancing their solubility. The ability of xanthate to form complexes with metal cations has also been used in the clean-up of contaminated mine water. Potassium ethyl xanthate was employed to remove copper ions from wastewater, with the high stability of the metal-xanthate complex resulting in low levels of leaching of the metal back into the environment even under acidic conditions (Chang et al., 2002). From these findings, Chang et al. (2002) suggested that these compounds in wastewater are not necessarily hazardous.

Xanthate salts are highly toxic to aquatic organisms especially when these are discharged directly to waterways (Qun Yan et al., 2011; Boening, 1998; Xu et al., 1988; Hawley, 1977; Webb et al., 1976). However, as indicated in the previous section, xanthates decompose rapidly in aquatic ecosystems (NICNAS, 1995; Xu et al, 1988; Read and Manser, 1975). Xanthate in the tailings slurry is thus not likely to persist in the acidic environment of tailings dam, as it normally decomposes relatively rapidly to ethanol, carbon disulphide and caustic soda in the tailings impoundment (NICNAS, 1995). Thus it is not generally transported to the surrounding environment where tailings are controlled within a well-constructed tailings dam (NICNAS, 1995).

This may imply that environmental risks of xanthate in receiving streams are minimal, as xanthates are unstable compounds and its toxicity may reflect the action of its degradation products. Much information on xanthate toxicity is in relation to its highly toxic intermediate products, which are also degradation products. Carbon disulphide in particular, is known to be deadly and cause nervous system damage and psychosis (Newhook et al., 2002; Smith and Timmerman, 2000). Therefore, the hazards and production process of carbon disulphide are reviewed in the next section.

2.2 Carbon disulphide description

The handling of and exposure to carbon disulphide poses the biggest human safety and health risk in the manufacturing of xanthate. This is due to its low flash point, and ignition temperature, as well as its acute toxicity (Harris, 2000). Carbon disulphide (CS_2) is an industrial chemical that is used in many applications. It is also produced as "an unintentional by-product of many combustion and high temperature industrial processes where sulphur compounds are present" (Smith and Timmerman, 2000). Commercial production of CS_2 began in the 1880 for mainly agricultural and solvent applications. Since the late nineteenth century, its uses have grown rapidly and it is now used in the manufacture of regenerated cellulose such as viscose rayon fibre and cellophane (currently the most common application), mining chemicals such as xanthates, as well as agricultural, pharmaceutical and rubber chemicals.

In 2010, approximately 72% of the global carbon disulphide consumption was reported to occur in Asia, with China being the highest consumer (49%), followed by India (13%) (IHS Chemicals, 2011). These countries use carbon disulphide mostly in the rayon fibre industries. Asia has become a centre for the production and consumption of carbon disulphide due to the global shift of large manufacturing industries relocating their production bases in this region. These include textile, rubber, as well as agricultural and mining chemical industries. The production capacity of carbon disulphide is expected to expand in future in this continent (4% annually between 2010 and 2015), due to the high demand by these manufacturing industries (IHS Chemicals, 2011). A large-scale production of carbon disulphide is greatly dependent on the access of raw materials, mainly natural gas and sulphur, and on modern production technologies (IHS Chemicals, 2011).

2.2.1 Carbon disulphide production

Charcoal-sulphur process

The original method for manufacturing carbon disulphide involves the reaction of sulphur and carbon (as shown previously in subsection 1.1.1, Equation 2) in the form of hardwood charcoal at temperatures in the range of 750–1000^{O}C.

$C + S_2 \rightarrow CS_2$

Two processes are used, the retort and electrothermal processes, with both processes requiring same raw material. The advantage of the electric furnace over externally fired retorts is that the source of heat is inside the walls of the furnace. It also has higher production capacities and has a longer operating life. However, it is a large consumer of

electrical energy (approximately 1000KWh/tonne of carbon disulphide), difficult to control, and requires more time for shutdown and clean-outs. Raw material and energy usages per kilogram of carbon disulphide product are approximately 0.92–0.95 kg sulphur, 0.22–0.25 kg charcoal, and 8.4–10.0 MJ (2000–2400 kcal) fuel (Smith and Timmerman, 2000).

Methane-sulphur process

As demand for carbon disulphide increased rapidly in the 1940s, limitations of the charcoal process provided the incentive for the development of a more efficient large-scale manufacturing method. The commercial use of hydrocarbons as the source of carbon was developed in the 1950s, and is still predominant worldwide today. This route uses methane from natural gas and sulphur as the feed-stock, and provides high capacity in an economical continuous unit. The chemical reaction (as shown previously in subsection 1.1.1, Equation 3) occurs at 570-620^{o}C

$$CH_4 + 2S_2 \rightarrow CS_2 + 2H_2S$$

A disadvantage of the methane–sulphur process is the formation of two moles of hydrogen sulphide by-product for every mole of methane reacted. However, technology for efficient recovery of sulphur values in hydrogen sulphide became commercially available at about the same time that the methane–sulphur process was developed.

The Claus process is the most significant process utilised for the recovery of sulphur from gaseous hydrogen sulphide produced in the CS_2 process. Part of the hydrogen sulphide is oxidised to form sulphur dioxide, which then reacts with the remaining hydrogen sulphide in the presence of a catalyst to form elementary sulphur. The overall chemical reaction (as shown in subsection 1.1.1, Equation 4) is strongly exothermic.

$$2H_2S + O_2 \rightarrow 2S^0 + 2H_2O_{\text{(steam)}}$$

Process heat, as well as condensation heat produced in this reaction, is utilised to produce medium and low pressure steam. With this efficient process unit, the methane–sulphur process is economically attractive.

In a modern carbon disulphide plant, all operations are continuous and automated. Raw material usages per tonne of carbon disulphide are approximately 310 m^3 of methane, or equivalent volume of other hydrocarbon gas, and 0.86–0.92 kg of sulphur, which accounts for a typical Claus sulphur recovery efficiency of about 95%. Fuel usage, as natural gas, is about 180 m^3/tonne carbon disulphide, excluding the fuel gas which is used for the incinerator or flare. The process is a net generator of steam; the amount depends on process design considerations (Smith and Timmerman, 2000).

The earliest method of producing carbon disulphide by the retort and electric furnace method is still used in locations where methane is unavailable or where small plants are economically viable. Currently, over 85% of the world's production capacity of carbon disulphide is based on methane. Other technologies for synthesis of carbon disulphide have been advocated, but none have reached a commercial scale (Lay et al., 2000).

2.2.2 Carbon disulphide properties and toxicity

Carbon disulphide is a toxic, dense liquid of high volatility and flammability. Industrial carbon disulphide is yellowish with an unpleasant odour. Anthropogenic releases of carbon disulphide to the environment occur exclusively as atmospheric emissions, with subsequent degradation by oxidation and hydroxylation. Carbon disulphide's atmospheric half-life is estimated at 1 to 10 weeks (Cox and Sheppard, 1980; Peyton et al., 1978)

Carbon disulphide released to surface waters in effluent streams is expected to partition rapidly to the atmosphere. This is due to high ratio of vapour pressure to solubility (Henry's law constant = 1.01×10^{-2} atm*m^3/mol) of the compound (ATSDR, 1996). Hydrolysis is not a significant removal mechanism since the evaporation half-life from a saturated solution is estimated to be 11 minutes (Peyton et al., 1978).

Carbon disulphide released to soils in spills is expected to volatilise rapidly, but a portion of the compound remaining on soil surfaces could be available for transport into groundwater since it does not have much affinity for soil particles (Farwell et al., 1979). It does not remain very long in water either because it evaporates within minutes. It is estimated that carbon disulphide is not taken up in significant amounts by aquatic organisms (EPA, 1986).

Exposure to carbon disulphide by humans is primarily confined to occupational situations. Inhalation is the principal route of exposure, although absorption through the skin is also important when the solvent is handled manually (WHO, 1979). Current permissible exposure limits (PELs) for carbon disulphide are 20 ppm as an 8-hour time-weighted average (TWA) concentration (OSHA, 1995).

An evaluation of toxicology effects on animals shows that exposure by inhalation causes significant toxicity to the brain, spleen, liver, and testes, and irritation of the intestinal tract in experimental animals (ATSDR, 1996). The oral LD_{50} in rats is 3 188 mg/kg, and a LC_{50} of 25 g/m^3 for two hours. The adverse exposure effects on humans include coronary heart disease, organic brain damage, and minor nervous system decrements. Exposure to 4 800 parts of carbon disulphide per million parts (ppm) of air for minutes results in coma and may cause death. Acute exposure to 160 to 230 ppm generally does not produce symptoms, and

exposure to 320 to 390 ppm is bearable for several hours before exposed workers develop headaches and feelings of malaise (ATSDR, 1996).

CS_2 is listed by the National Occupational Health and Safety Commission (NOHSC) Australia, under a list of designated hazardous substances as 'Toxic' at concentrations above 1%. These causes danger of serious damage to health by prolonged exposure through inhalation, possible risk of impaired fertility, possible risk of harm to the unborn child and irritation to eyes and skin. Solutions containing less than 1%, but greater than 0.2% CS_2 are classified as 'Harmful' (NOHSC, 1999). In South Africa CS_2 is listed by the National Environmental Management (NEM): Air Quality Act, with a minimum emission standard of 150mg/Nm^3, under normal conditions of 6% oxygen, 273 K and 101.3Kpa (NEM, 2010).

Table 2 shows a summary of epidemiological studies on carbon disulphide (NICNAS, 2000). A number of the epidemiological studies indicate that some workers may have been exposed to levels of CS_2 lower than the recommended exposure standard, and the majority of these studies are backdated in nature and as a result, they do not provide adequate dose response data for critical effects (NICNAS, 2000).

Table 2: Summary of epidemiological reviews on carbon disulphide (NICNAS, 2000)

Industry (Country)	Number of exposed workers	Adverse health effect(s)/findings	CS_2 monitoring	Reference
Viscose/rayon (Belgium)	120	**Neurological effects** (polyneuropathy)	3 - 147 mg/m^3 (1 – 47 ppm)	De Fruyt et al. (1998)
Occupational case studies (Korea)	34	**Neurological effects** (reduced cerebral blood flow)	Not stated	Lee and Kim (1998)
Rayon (Japan)	432	**Neurological effects** (reduced nerve conduction velocities) **Ophthalmological effects** (microaneurysm) (>2:1 vs control) **Endocrine effects** (increased glycosylated haemoglobin)	No air sampling. 25% urine samples > 5 mg/g TTCA*.	Omae et al. (1998); Takebayashi et al. (1998)
Viscose/ cellophane processing (Japan)	118	**Cardiovascular effects** (ECG abnormalities) (>4:1 vs control)	Up to 170 mg/m^3 (55 ppm)	Kuo et al. (1997)
Viscose/rayon (Poland)	188	**Neurological effects** (alpha rhythm frequency)	10-42 mg/m^3 (3 – 13 ppm) (mean annual data)	Sinczuk-Walczak & Szymczak (1997)
Xanthate mining workers (Australia)	200 (estimate)	**Cardiovascular disease.** Retrospective mortality study (based on data from Nurminen et al., 1982 for Finnish viscose workers). Estimated 1.28 extra deaths per year in mining workers due to CS_2)	Not stated	Christophers and Zammit (1997)
Synthetic fibres (Poland)	119 (F)	**Endocrine and reproductive effects** (increased spontaneous abortion; decreased serum estradiol and progesterone and increased serum testosterone, prolactin & serotonin).	9 – 23 mg/m^3 (3 – 7 ppm)	Pieleszek (1997). Kuligowski (1996).
Viscose (Germany)	247 (M)	No adverse **neurological or cardiovascular effects**.	<0.2 – 65.7 ppm (0.6 - 204 mg/m^3) (median: 4 ppm/12 mg/m^3)	Reinhardt et al. (1997); Drexler et al. (1995a,1996)
Viscose/rayon (USA)	Historical data (NIOSH database)	**Ischaemic heart disease**. No excess risk of mortality below 20 ppm. Benchmark concentration of 16 - 18.5 ppm derived for early **neurological effects** (nerve MCV and amplitude ratio).	Historical data	Price et al (1996, 1997)
Viscose/rayon (Belgium)	43-123	**Hepatic effects** (increased GGT) **Cardiovascular effects** (increased blood pressure); **Neurological effects** (polyneuopathy - significant < 10 ppm); **Ophthalmological effects** (microaneurysm - significant > 10 ppm); **Reproductive effects** (significant effects on libido/potency – no effects on fertility)	4 - 112 mg/m^3 (1 – 36 ppm)	Vanhoorne et el. (1992, 1994, 1995, 1996)
Not stated (Poland)	114	**Neurological effects** (CNS – cortical atrophy); **Cardiovascular effects** (increased cholesterol);	0-65 mg/m^3 (0 – 21 ppm)	Chrostek Maj & Czeczotko (1995)
Viscose/rayon (China)	163	**Neurological effects** (polyneuropathy in 13-53% workers)	40-67 ppm (124 – 208 mg/m^3)	Chu et al (1995)
Viscose/rayon (Italy)	493	**Neurological effects** (behavioral disturbance at levels <8 mg/m^3)	Historical data	Cassitto et al (1993)

* biological exposure index for CS_2 adopted by ACGIH
F= females
M = Males

Note : See original article for references

2.3 Xanthate use for ARD mitigation

Xanthates are widely used in the mining industry as mineral collectors for the recovery of metal sulphides from ore slurries in a flotation process (Wills, 2011). This application was first introduced by Keller (1927). Besides being used in the beneficiation of metal-bearing ores, xanthate salts have also been found to be effective when used in the desulphurisation flotation process for the mitigation of acid mine drainage (AMD), also referred to as acid rock drainage (ARD), which is a significant environmental problem in the mining industry.

The following subsections (2.3.1 and 2.3.2) briefly elaborate on the general treatment of mine waste (tailings slurry) generated by milling and flotation, the disposal of this waste to tailings impoundments as well as the generation of ARD from the tailings impoundments and available methods developed to predict the ARD potential (subsection 2.3.1). Subsection 2.3.2 describes in more detail the proposed desulphurisation flotation process for the mitigation of ARD using xanthate.

2.3.1 Mine waste and acid rock drainage

Mine waste (tailings slurry) generated by flotation is normally thickened prior to disposal, with the thickener overflow being recycled back to the mill circuit. The tailings slurry is then discharged to specially designed impoundments, where more water can be recovered and recycled back to the mill. This conventional management method is explained in detail in Chapter 5.

Acid rock drainage formation

The most serious and persistent environmental problem from the disposal of mine waste is the continued generation of acid drainage from sulphide bearing waste, where leachate generation occurs as a result of percolating water coming into contact with the solid waste (Figure 3).

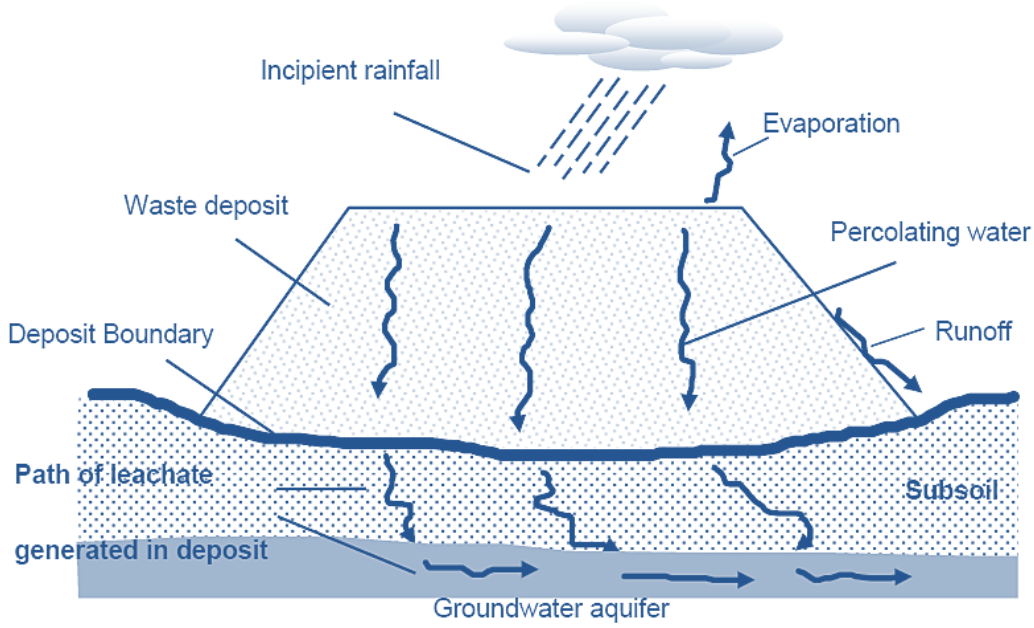


Figure 3: Leachate generation and transport from a solid waste disposal site (Hansen, 2004)

ARD refers to acidic discharge, below pH 6, formed through weathering of sulphide minerals, particular pyrite (FeS_2), which is the most common and concentrated sulphide

mineral in mine wastes generated from the processing of sulphide ores. ARD is normally associated with human activities particularly mining and processing of sulphide mineral-bearing ores. For example, in impoundments of copper tailings slurries, exposure of the sulphide mineral (FeS_2), to oxygen and pore water arising from the tailings material, results in the oxidative dissolution in accordance with the reactions in Equation 12-14.

$$2FeS_2 + 7O_2 + 2H_2O \rightarrow 2Fe^{2+} + 4SO_4^{2-} + 4H^+ \quad \text{Equation 12}$$

$$4Fe^{2+} + O_2 + 4H^+ \rightarrow 4Fe^{3+} + 2H_2O \quad \text{Equation 13}$$

$$FeS_2 + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \quad \text{Equation 14}$$

The primary reactions of acid drainage (Equation 12, 13 and 14) involve the oxidation of the sulphide mineral (FeS_2), and the subsequent release of ferrous iron (Fe^{2+}), sulphate (SO_4^{2-}) and hydrogen (H^+) into tailings pore water. Iron and sulphur oxidising bacteria, catalyse the oxidation of ferrous to ferric iron (Equation 13), which is a more effective oxidant of sulphide minerals than oxygen (INAP, 2009). The oxidation of ferrous ion to ferric ion (Equation 13) and that of pyrite by ferric ion to produce ferrous (Equation 14) form a continuous cycle (Lottermoser, 2010).

Carbonate minerals, such as calcite, found in the sulphide material, are the most important neutralising minerals in base metal sulphide tailings deposits. This is particularly the case in the short-medium terms, as they are highly reactive. Acid neutralising dissolution reaction of the calcite is as follows:

$$CaCO_3 + H^+ \rightarrow Ca^{2+} + HCO_3^- \quad \text{Equation 15}$$

Concentrations of the calcite become depleted as the oxidation rate of sulphide increases. However, this can vary quite significantly and is dependent on a number of factors, particularly the composition and mineralogy of the tailings with regards to the relative concentration of sulphide and acid neutralising minerals.

Apart from the primary acid generating and acid neutralising reactions described above, the final pH and compositions of leachate generated from sulphide wastes is governed by secondary reactions, particularly the formation of secondary iron hydroxides (Equation 16) and oxysulphates, as well as gypsum, which influences the sulphate concentration and not the pH (Lottermoser, 2010).

$$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_3 + 3H^+ \quad \text{Equation 16}$$

Environmental implications

A lowering of the pH of the pore water through the generation of acid results in an increase in the mobilisation of metals. For example, in a complex porphyry-type ore, heavy metals dissolved by the acid generated include aluminium, manganese, copper, zinc, nickel, iron and cobalt (Broadhurst et al, 2007b). Trace metals such as arsenic are also mobilised which can cause enrichment in mine water to toxic levels (Broadhurst, 2007a). In her PhD thesis, Broadhurst (2007a) modelled the likely availability of metals (presented in Appendix A) for release into the environment using thermodynamic models and typical pH and sulphate concentrations in pore water for porphyry-type copper sulphide tailings deposits. The results indicated that salinity and the metals manganese and iron are most likely to be of environmental significance for this type of tailings. Other components including arsenic, zinc, cadmium, boron, molybdenum, selenium and, to a lesser extent nickel, cobalt, antimony and silicon may also be of environmental significance, depending on their specific feed ore concentrations.

In another study, Hesketh (2010a) investigated the availability of metals from a porphyry copper sulphide tailing sample under biokinetic leach conditions, which entails leaching with an acidic (pH 2) salt solution in the presence of iron and sulphur oxidising bacteria. His results indicated that manganese (Mn) was the only element that posed a significant environmental risk. Trace elements (e.g. arsenic, molybdenum, cadmium, cobalt, silver, and palladium) and minor elements (e.g. nickel, chromium, and zinc) displayed low or negligible environmental risk under the test conditions.

The environmental impacts of ARD have been described in detail in previous work (e.g. Van Damme et al., 2008; Broadhurst, 2007a; Broadhurst et al., 2007b; Valente and Gomes, 2007; Gray, 1997; Ripley and Redman, 1995). These studies have shown that the release of this contaminated leachate can have adverse effects on surrounding environments more especially on water quality and consequently the usability of water sources (surface and ground water). These effects in turn lead to ecotoxicity and human toxicity (Jennings et al., 2008; Blowes et al., 2005). ARD effects are mainly due to the acidity itself, metal toxicity, which is dependent on speciation, and salinisation (Broadhurst et al., 2007b). In affected rivers, microinvertebrates found downstream of ARD discharges are the most sensitive indicators of metal contamination (Van Damme et al., 2008). The contaminated leached also affects agricultural land use in surrounding areas.

ARD prediction

A number of geochemical tests have been developed for predicting the ARD potential of solid wastes. These are generally classified as either static or kinetic methods. Static tests

such as the acid base accounting (ABA) and net acid generation (NAG) methods are relatively simple methods and are used to classify samples according to their acid neutralising and acid forming characteristics. In the ABA test, the net amount of potential acid produced by a mine waste, or the net acid production potential (NAPP), is calculated as the difference in the maximum potential acidity (MPA) and acid neutralisation capacity (ANC). Units of measurement are typically expressed in mass (kg, metric tonne, etc.) as acid (H_2SO_4) per tonne of waste, or as calcium carbonate ($CaCO_3$) per 1000 tonnes of waste (Stewart et al., 2006).

NAPP = MPA – ANC

If the difference between MPA and ANC is negative, then the potential exists for the waste to be non-acid forming; if positive, there may be a risk of acid formation.

The MPA is calculated based on the sulphur grade of the sample, assuming that all the sulphur in the sample is in a form available for acid production, i.e. pyrite. The ANC is determined empirically by reacting the sample with hydrochloric acid (HCl) to dissolve available acid consuming minerals such as carbonates. ANC can also be estimated from the calcite concentration, in cases where this is the major neutralising mineral. Kinetic tests attempt to mimic natural oxidation and weathering reactions in the field. They are often conducted to confirm results of static tests and are intended to simulate the time-related behaviour of the acid-forming and acid-neutralising reactions. A number of kinetic tests are used, such as the biokinetic shake flask test (Hesketh, 2010b), the humidity cell test (Sobek et al., 1978) and leach column tests (Benzaazoua et al., 2004). However, a detailed review of these tests is beyond the scope of this project.

ARD mitigation

There are different techniques used to limit the release of ARD into the environment. These are called source control methods. Basically, these methods try to limit the availability of one or more of the components (water, oxygen, or sulphides) necessary for the generation of acidity. To limit the penetration of water into the tailings, covers made of low hydraulic conductivity soils or synthetic materials (geomembranes or bentonite geocomposites) can be used (Bois et al., 2005). To limit oxygen migration into a mine tailing impoundment, different techniques are available. A water cover can be placed over reactive tailings to reduce oxygen availability (Simms et al., 2000), or oxygen-consuming materials can be used as covers, e.g. wood waste, straw mulch or other organic residues (Cabral et al., 2000). Another alternative is to use natural materials or non-acid generating mine tailings having capillary barrier effects (CBE), which have a high moisture-retention capacity to prevent oxygen migration (e.g. Ricard et al., 1997). However, the long-term effectiveness of covers

for the removal of ARD risks has yet to be proven. A more reliable ARD mitigation approach is to generate wastes that are benign in the first-place, through the pre-disposal removal of sulphide minerals. This approach is discussed in the following subsection.

2.3.2 Desulphurisation flotation for ARD mitigation

Pre-disposal removal of sulphides, most commonly pyrite (FeS_2), eliminates the potential for the production of ARD from sulphide minerals (Cilliers, 2006). Desulphurisation flotation has been found to be an attractive alternative to conventional prevention techniques for the mitigation of ARD (Kazadi Mbamba et al, 2012; Harrison et al., 2010; Hesketh et al, 2010c; Bois et al., 2004; Benzaazoua and Kongolo, 2003; Benzaazoua et al., 2000). This technique is based on the same principle as conventional pyrite flotation from milled run-of-mine ores, i.e. standard flotation circuits. This process when placed at the end of a primary treatment circuit, greatly reduces the ARD risks by concentrating a small volume of sulphide-rich tailings fraction which can be converted into useful by-products and a large volume of sulphide-lean tailings fraction which can be disposed of without posing an ARD risk. Figure 4 demonstrates a conceptual approach of the desulphurisation process as proposed by Hesketh et al. (2010c). This process is explained in length in Chapter 5 of the thesis.

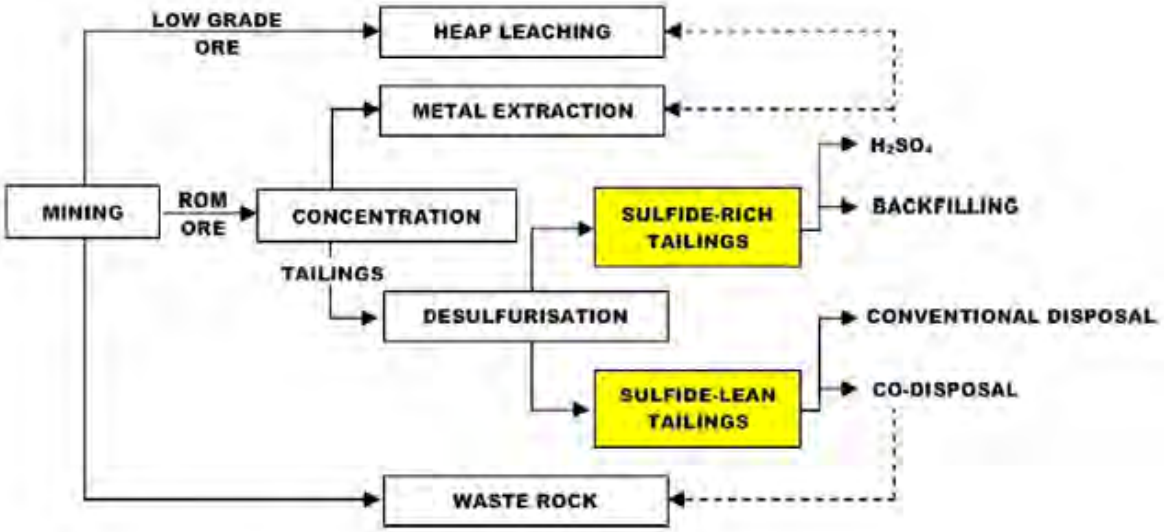


Figure 4: Conceptual approach to sulphide tailings management (Hesketh et al., 2010c)

Xanthate-based collectors have been the most commonly used reagents in desulphurisation flotation studies, as they are characterised by their ability to collect sulphide minerals in general. The length of their radical chain is the reason for their high selectivity (Crozier, 1992). Other collectors used successfully for desulphurisation flotation include mercaptobenzothiazoles (O'Connor and Dunne, 1991), thiocarbamates (Bradshaw and O'Connor, 1994), amines (Hodgkinson et al., 1994) and dithiophosphate (Hesketh, 2010a).

However, a comparative study by Benzaazoua (2000) and a subsequent study by Benzaazoua and Kongolo (2003) showed that xanthates result in faster flotation kinetics and are more cost effective than other sulphide collectors, including dithiophosphates, dithiocarbamate and phosphorodithioate salt.

Whilst studies have been conducted on the use of xanthates for the desulphurisation flotation of wastes arising from the processing of both coal (Kazadi Mbamba et al., 2012) and hard rock ores, the focus of this study is on hard rock ore, and specifically base metal, tailings. A summary of the various desulphurisation flotation studies on hard rock ore tailings, using xanthate salts as a collector, is presented in Table 3.

Table 3: Summary of literature results of desulphurisation flotation of hard rock ore tailings, using xanthate as a collector

Valuable metal	S (wt %)		S extraction (%)	Collector dosage (g/tonne)	Collector type	Reference
	Before desulphurisation	After desulphurisation				
Zn, Cu, Ag,Au (G)	24.2	1.68	91	80	Potassium amyl xanthate (KAX-51)	Benzaazoua et al. (2000)
Zn,Cu, Ag, Au (M)	16.2	1.92	84	60		
Au, Cu (P)	2.9	2.08	31	10		
Cu, Zn	9.38	0.86	90.8	90	Potassium propyl xanthate (KAX-41)	Benzaazoua and Kongolo (2003)
Cu, Zn	5	0.51	89.8	25		
Cu, Zn	20	0.5	98.8	100	Potassium amyl xanthate (KAX-51)	Bois et al. (2005)

Optimum xanthate dosages for these ores varied from 10 g/tonne at low sulphide content (2.9% S) to 100 g/tonne for tailings with higher sulphide content (20% S). Sulphur removal was mostly above 80%, and results indicated low residual sulphur in desulphurised tailings (<2% S).

Collector dosage has an effect on the desulphurisation flotation process. In the study presented by Benzaazoua et al. (2000), four pulps which contained different sulphur concentrations were studied using xanthate and amine acetate collectors. The kinetic curves for each tailing flotation studied showed that further increase above 140g/tonne in the collector dosage did not improve sulphide recovery and low concentrations seemed to have little or no effect on sulphide recovery (Figure 5).

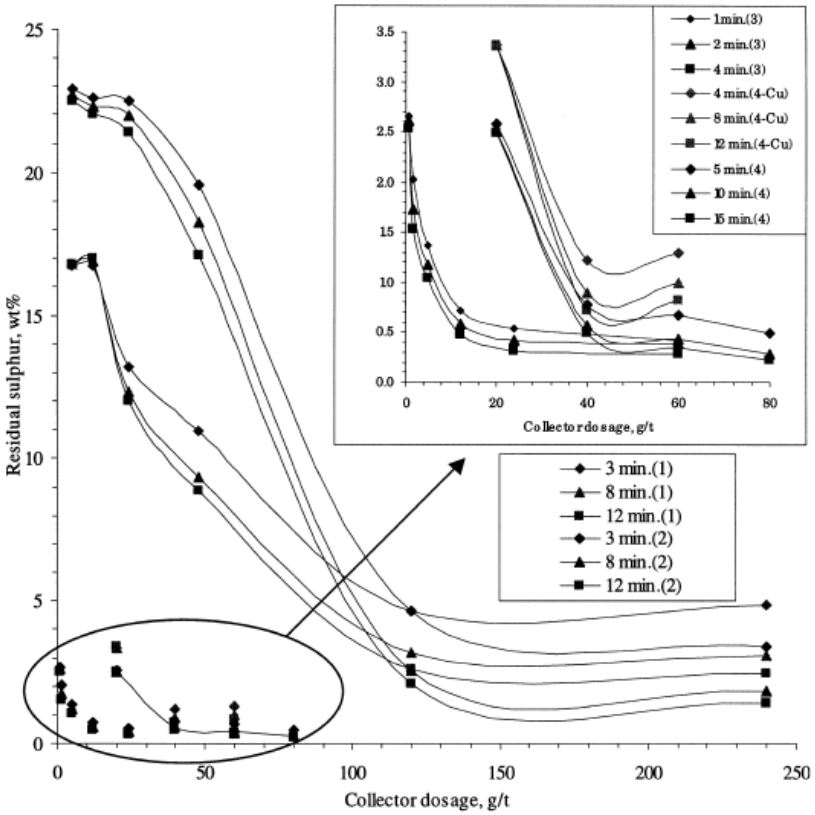


Figure 5: Collector dosages vs. residual sulphur in the tailings after various flotation times corresponding to four pulps studied (Benzaazoua et al., 2000)

Desulphurisation flotation has been conducted to verify its continuous feasibility at a mine site by performing tests on a pilot plant scale using potassium amyl xanthate (KAX 51) (Bois et al., 2005). These tests demonstrated good sulphide recoveries very low sulphide grade in the desulphurised tailings, confirming that tailings can be desulphurised using the pilot plant.

Besides being environmentally effective, desulphurisation has also proven to be an economically attractive in comparison to other tailings management methods. In the study presented by Bois et al. (2005), estimated costs were compared for different tailings management options (Figure 6). Desulphurisation (complete and partial) indicated to be a viable economic option because of the lower construction costs involved. Cover with capillary barrier effect (CCBE) showed to be more expensive due to costly construction materials, whilst underwater disposal costs were attractive, but dependant on site topography.

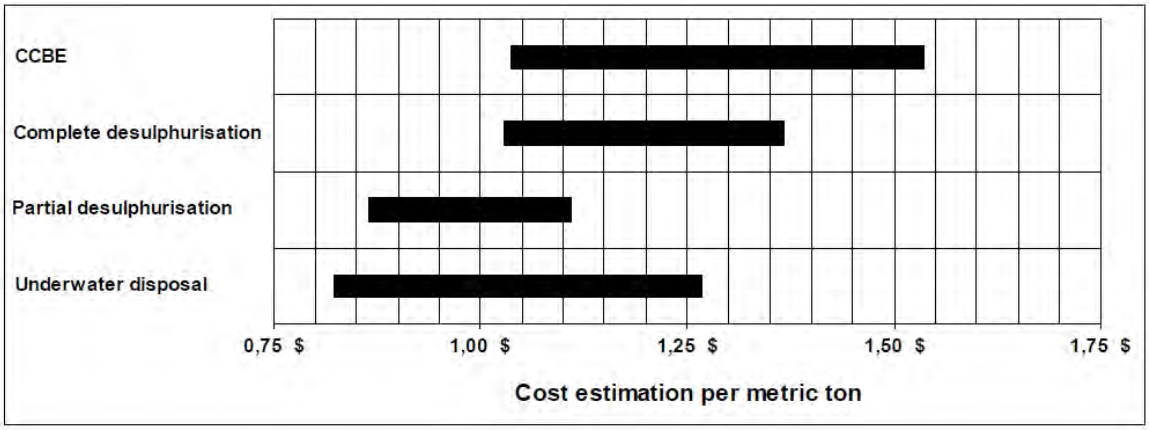


Figure 6: Comparison of cost estimations of desulphurisation compared with other ARD prevention methods (Bois et al., 2005)

Xanthate performance in the desulphurisation flotation process for ARD mitigation in most of the studies reported in the literature has only been based on the ARD generation of the final tailings, with little consideration being given to the potential environmental harmful effects of the residual flotation reagents (particularly xanthates) or other metals in the desulphurised tailings.

2.4 Life cycle assessment (LCA)

The use of LCA is gaining widespread acceptance in industries as more companies are engaging in greener products and using greener processes. This tool has support from the international community; the Society of Environmental Toxicology and Chemistry (SETAC), which published earlier guidelines on LCA, the International Standards Organisation (ISO), which further developed methodological standards (the most recent versions were published in 2006), and the United Nations Environment Programme (UNEP). In 2002, SETAC joined forces with UNEP to launch the Life Cycle Initiative which was formulated in putting life cycle thinking into practice and improving supporting tools through better data and indicators (SAIC and Curran, 2006). Currently on phase III, (2012-2016) which is a build-up on the successes of activities since 2002, Life Cycle Initiative's key objective for this phase is to mainstream the use of life cycle approaches (e.g. accessibility to cost-effective, robust methodologies and tools based on reliable data) (http://www.lifecycleinitiative.org, 2014). This Phase also involves an important innovation of the assessment of water use which has traditionally received very limited attention in LCA (Milà i Canals et al., 2009; Jefferies et al, 2012). The development of inventory guidelines and new impact assessment methods for water use is currently making considerable progress (http://www.lifecycleinitiative.org, 2014). Parallel to this, the International Organisation for Standardisation has recently (2014) published an international standard for water footprint based on LCA (ISO 14046).

ISO (the International Organisation for Standardisation) provides the following procedural definition for performing an LCA.

> "LCA is a technique for assessing the environmental aspects and potential impacts associated with a product by: compiling an inventory of relevant inputs and outputs of a product system, evaluating the potential environmental impacts associated with those inputs and outputs and interpreting the results of the inventory analysis and impact assessment phases in relation to the objectives of the study" (ISO 14040, 2006).

LCA takes into account the environmental aspects and potential impacts of the entire life cycle of a product from cradle to grave i.e. from raw materials acquisition through production, use and disposal (SAIC and Curran, 2006; Guinée et al., 2001). It can also be used to analyse systems from cradle-to-gate (raw material acquisition and production), gate-to-gate (production) and gate-to-grave (product use and disposal), depending on the problem definition. The life cycle inventory quantitatively describes natural resources into and emissions out of the product's life cycle system as shown in Figure 7. Impacts such as climate change, acidification, ozone depletion, eutrophication, ecotoxicity, human toxicity, natural resource depletion, and land use are typically characterised during life cycle impact assessment.

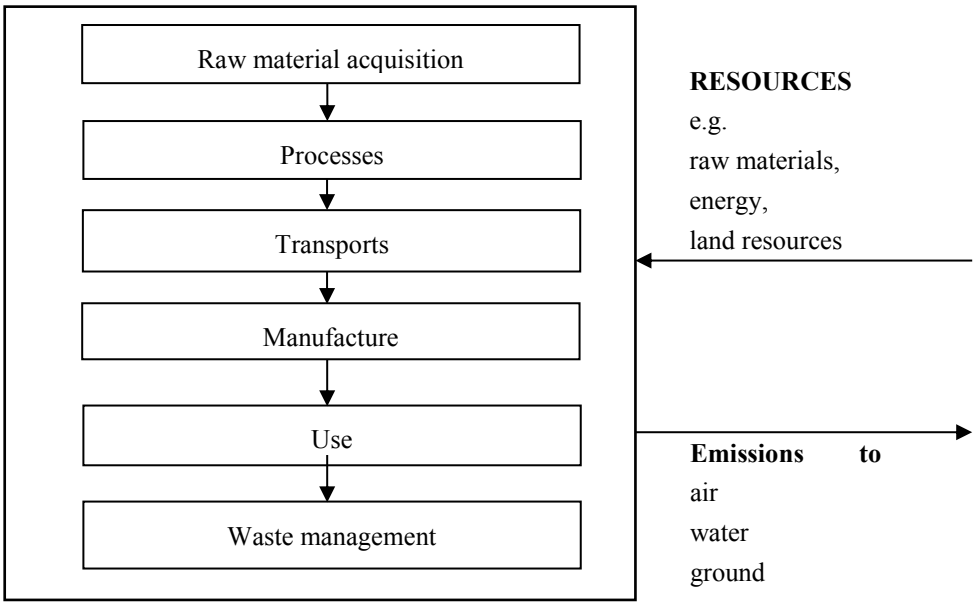


Figure 7: The life cycle model after Baumann and Tillman (2004)

The next subsections (2.4.1 and 2.4.2) discuss the procedural framework for conducting an LCA study according to the ISO standards and the different available models that have been developed to model the environmental impacts.

2.4.1 LCA procedural framework

The LCA framework describes the whole procedure for how such a study is performed and interpreted.Technical guidelines and procedures are provided by the ISO standards. According to ISO 14040 standards, an LCA should consist of four methodological stages, performed in the following order:

1. *Goal and scope definition*

This stage explicitly defines the goal of the project (product, process or activity) by stating the intended application, reason and audience of the study (ISO 14040, 2006). The scope includes an elaboration of the functional unit (basis of comparison), system boundary, data requirements, assumptions and limitations that may exist for the study (ISO 14040, 2006). Based on the goal and scope of the study, it is extremely important that a precise definition of the system boundary is stated. For example, the life cycle of processes can be eliminated from system boundaries when they are common in processes under comparison, ensuring that data sets remain manageable (Stewart and Petrie, 1999). It is also useful for comparative life cycle assessments to consider a distinction between foreground and background systems (Tillman et al 1998; Clift et al., 1998). In accordance with Tillman (2000): "The foreground system is the collection of processes on which measures may be taken concerning their selection or mode of operation as a result of decisions based on the study. The background system consists of all other modelled processes influenced by measures taken in the foreground system".

2. *Life cycle inventory analysis (LCI)*

This step involves data collection and quantification of the inputs (energy, materials) and outputs (emissions and waste) of the system under study, in relation to the functional unit and requirements of the project's defined goal and scope (ISO 14040, 2006; Bauman and Tillman, 2004)

3. *Life cycle impact assessment (LCIA)*

The LCIA step evaluates the potential human and ecological effects of the inputs and outputs identified in the inventory analysis by associating it with specific environmental impacts categories and indicators to get a better understanding of these impacts (ISO 14040, 2006). This step deals with intensive amounts of data from the inventory analysis step, and consists of four analysis stages or sub-steps:

- *Classification*: substances are sorted into classes according to the effect they have on the environment.

- *Characterisation*: substances are multiplied by a characterisation factor (CF) which reflects their relative contribution to the environmental impact.
- *Normalisation*: the quantified impact is compared to a certain reference value.
- *Weighting*: different value choices are given to impact categories to generate a single score.

In accordance to ISO 14040, (2006) classification and characterisation steps are mandatory steps while normalisation and weighting are optional steps. Impact category indicator results can be chosen either at the midpoint or endpoint level. For example, Figure 8 shows how some midpoint effects map to their respective endpoints effects (Jolliet et al., 2003).

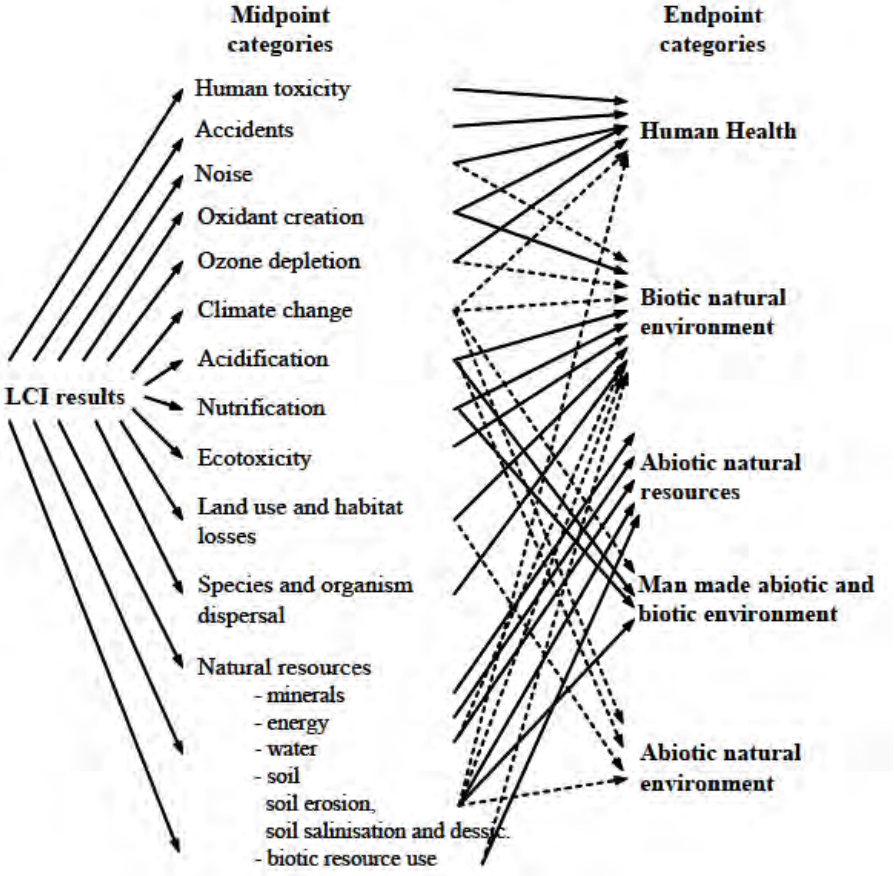


Figure 8: General structure of the LCIA framework (Jolliet et al., 2003) Where: solid arrows indicate that a quantitative model is available; dashed arrows indicate that only uncertain or qualitative relationships are known.

The midpoint impact category converts inventory data into environmental impacts (e.g. CH_4 into global warming potential). The endpoint impact category converts impacts into damages (e.g. global warming potential into human health damage). The midpoint approach allows a transparent analysis of environment impacts with relatively low uncertainties; however, these categories are rather difficulty to communicate to the decision makers. Endpoint results are

less numerous (fewer impact categories to consider) but the models are no less detailed. They are usually easier for decision makers to relate to, but midpoint probably easier to understand (simpler calculations underlying them). Available LCIA methods are discussed in more detail in subsection 2.4.2 below. These methods are mostly developed by academic research groups and are available in scientific publication and sometimes published on websites (e.g. ReCiPe and IMPACT 2002+).

4. Interpretation

The final step in the LCA procedure evaluates the findings of the inventory analysis and impact assessment steps which are based on a relative approach. Conclusions and recommendations are provided in a way that is meaningful within the context of the study's defined goal and scope (ISO 14040, 2006). Improvements to reduce the identified system's environmental impacts are also evaluated. Sensitivity analysis can be performed to determine the robustness of the overall LCA results influenced by assumptions in the data used (Guinée et al., 2001).

The above-mentioned steps are considered to be interactive and iterative in nature and often the goal and scope of the LCA study is revisited if uncertainties and a need for clarity occur in the other stages (ISO 14040, 2006; Bauman and Tillman, 2004).

2.4.2 Impact assessment methodologies

Different methodologies have been developed to study and capture more accurately the environmental impacts, typically making the modules more complex. As highlighted under section 2.4.1 (Life cycle impact assessment), LCI results are classified within impact categories and indicators, which can be chosen at the midpoint and endpoint level.

Earlier LCIA methodologies that only took into account the midpoint approach include CML, developed by the Institute of Environmental Science of the University of Leiden in the Netherlands, EDIP (Environmental Design of Industrial Products), developed at the Danish Technical University, and TRACI (Tool for the Reduction and Assessment of Chemical and other environmental Impacts), developed by the Environmental Protection Agency (EPA) in the USA. Each of these methodologies typically provides for a number of environmental impact categories to be included, which can, however, only be applied through LCI once classification factors are available.

Methodologies that are only based on the endpoint approach include Eco-Indicator 99 methodology, developed under the Dutch NOH programme by Pré Consultants, EPS 2000 methodology (Environmental Priority Strategies in product design), Eco Scarcity that was

released in Switzerland and JEPIX (Japan Environmental Policy Priorities Index), which based on the Eco Scarcity methodology. These methodologies model the environmental impacts up to the different environmental areas of protection considered.

In 2002, the Life Cycle Initiative (Partnership between SETAC and UNEP) proposed that the midpoint and endpoint approaches could be combined in a single LCIA method. Such methods were recently made available which include: ReCiPe, developed by PRé Consultants, CML, RIVM and Radboud University Nijmegen (Goedkoop et al., 2009); IMPACT 2002+, developed by the Swiss École Polytechnique Fédérale De Lausanne (EPFL) institutes of technology (Jolliet et al., 2002); and Lime, a Japanese methodology (Itsubo and Inaba, 2003).

The development of some of the more commonly used LCIA methodologies is illustrated in Figure 9.

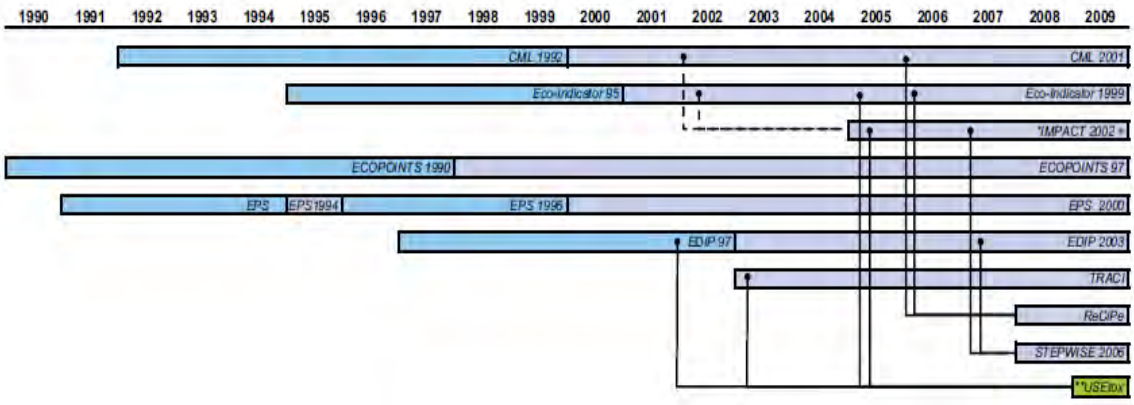


Figure 9: Development of some of the different existing methodologies over time. The black connectors show the genealogy of the methodologies (e.g. ReCiPe originated from the previous CML 2001 and Eco-indicator 99) (Pizzol et al., 2011b)

ReCiPe is one of the most recent and harmonised life cycle impact assessment methods. The advantages of ReCiPe method relative to other methods is that it considers the largest set of midpoint impact categories and having both midpoint and endpoint approaches, one can freely choose where to end his analysis. The method addresses global environmental impacts where possible, and unlike other methods (Eco-indicator 99, EPS, Lime and IMPACT 2002+) the impact assessment assumes that potential impacts from future extractions have already been included in the inventory analysis. ReCiPe considers eighteen midpoint categories; these are climate change, ozone depletion, terrestrial acidification, freshwater eutrophication, marine eutrophication, human toxicity, photochemical oxidant formation, particulate matter formation, terrestrial ecotoxicity, freshwater ecotoxicity, marine ecotoxicity, ionising radiation, agricultural land occupation, urban land occupation, natural land transformation, water depletion, mineral resource depletion, fossil fuel depletion. The endpoint level

addresses three categories, which are damage to human health, damage to ecosystem diversity and damage to resources availability.

Another recently developed LCIA method is USEtox, which has been developed through a process of comparison and harmonisation of other existing models (EDIP 97, Traci, Eco-Indicator 99 and Impact 2002) for characterisation of only human and ecotoxicity impacts. This rather sophisticated method calculates a chemical's hazard characteristics by taking into account its toxicity, its fate and its exposure. It has been evaluated by the UNEP/SETAC group of experts in collaboration with teams behind current models, who created the new scientific consensus multimedia model, which is intended to form a basis of future recommendation on characterisation of toxic impacts (Rosenbaum et al., 2008; Hauschild et al., 2008). It consist a list of about 3 000 characterisation factors for chemicals, making it the largest substance coverage presently available, and the uncertainty of the model has been quantified, therefore representing an improved application of human health and ecotoxicity characterisation factors in LCA (Rosenbaum et al., 2008).

LCIA methodologies are used with specific software tools. One of the most widely used LCA software tool is SimaPro, created by PRé Consultants (2012). This tool contains several impact assessment methods and several inventory databases, which can be edited and expanded without limitation. It can compare and analyse complex products with complex life cycles (PRé Consultants, 2012). Other popular models used are: GaBi, supported jointly by PE Europe GmbH and IKP University of Stuttgart (www.gabi-software.com, 2013) GEMIS, from the Öko-Institut's (www.oeko.de/service/gemis/en/, 2013), and BEES, created by the National Institute for Standards and Technology (NIST) Building and Fire Research Laboratory (www.nist.gov/el/economics/BEESSoftware.cfm, 2013).

2.5 LCA applications and limitations

LCA can be applied in different categories i.e. in products and services, in process selection, design and optimisation (Azapagic, 1999; Azapagic & Clift, 1999). In general, LCA is applied to products for comparative assessment and optimisation of the final product. Its application to processes is not as common as LCA of products. Application of LCA to products is usually for marketing and policy purposes (Burgess and Brennan, 2000), while application to processes is for ecodesign, and the comparison and selection of the most environmental friendly process (Chevalier et al., 2003). However, as pointed out by Chevalier et al. (2003), "the LCA of processes requires the LCA of products and vice versa. Both of the approaches are essential and inseparable" (Chevalier et al., 2003). The following subsections, however, focus on the application of LCA in two process industries viz. chemical process

industry (subsection 2.5.1) and the mining and mineral beneficiation industry (subsection 2.5.2). The limitations of LCA, in so far as they are relevant to this study are described in subsection 2.5.3.

2.5.1 Application in the chemical process industry

Several studies have applied LCA on some chemical processes (e.g., Kim and Overcash, 2003; Jiménez-González et al., 2000; Jiménez-González et al., 2004; Wernet et al., 2010). In all the instances, gate to gate life cycle inventories were collated for databases of chemical substances processes, and subsequently used to support LCA of final products. Moreover, LCA has also been used for comparative chemical processes. Table 4 below summarises some of those studies, by reflecting on processes compared, and in relevant cases for which products.

Table 4: Examples of comparative LCA applied to processes in the chemical industry

Author	Processes compared	Product	Impact categories assessed
Furuholt (1995)	Three fuel production processes	Regular gasoline, gasoline with MTBE and diesel	Global warming potential, photo-oxidant formation, eutrophication, acidification, consumption of fossil energy, waste generation
Vigon et al., (1996)	Conventional hydrocarbon and biomass feedstock based processes	1,4-butanediol	Fourteen impact categories including Global warming potential and fossil fuel consumption
Koroneos et al., (2004)	Conventional sources (natural gas steam reforming) and renewable sources (solar, wind hydro and biomass)	Hydrogen fuel	Global warming potential, acidification, eutrophication, winter smog effect
Portha et al., (2010)	Naphtha catalytic reforming (Basic and modified process)	Reformate	Fossil fuels consumption, climate change, respiratory effects

The comparison of these processes was based on a cradle-to-gate approach and the differences in environmental impact categories selected in each study can be attributed mainly to the goal and scope of the study, as well as the different material used in the processes. Global warming potential and resource depletion impacts were accounted for in all the studies (Table 4), as these impacts are associated with energy consumption (which is common to all processes).

2.5.2 Application in the mining and mineral beneficiation sector

LCA has been used in the mining and mineral processing since the mid to late 1990s. It was used for various applications which were mostly focusing on building up life cycle inventory

(LCI) databases for metal production processes, which could subsequently be used to support life cycle assessments of consumer products. Table 5 gives an example of a number of studies that have been published since the year 2000 pertaining to the application of LCA in the mining and mineral beneficiation industry. Most of these studies were performed to determine the environmental impacts of various metals production processes.

Table 5: Examples of LCA application in the mining and mineral beneficiation industry

Author	Description	Impact categories assessed
Norgate and Haque (2010)	Cradle-to-gate life cycle of the mining and processing of iron ore, aluminium and copper concentrate	Gross energy requirement and global warming potential
Norgate et al. (2007)	Assessment of the cradle-to-gate environmental impacts of commercial or developmental metal production processes (copper, nickel, aluminium, lead, zinc, steel, stainless steel and titanium) in Australia.	Global warming, acidification, gross energy requirement, solid waste burden
Mangena and Brent (2006)	Cradle-to-gate LCA study of coal production from four mine sites in South Africa	Acidification, land and water use, eutrophication, ozone depletion, global warming, mineral and energy depletion, human, aquatic and terrestrial toxicity,
Suppen et al. (2006)	Overview of Mexican mining industry and strategies being implemented to incorporate sustainable development principles, including the development of a national base metals life cycle inventory	Environmental impacts from resources, materials, energy use as well as air, water and solid waste emissions
Tan and Khoo (2005)	Assessment of the environmental life cycle of primary aluminium, from mining to its final production.	Global warming potential, acidification, human toxicity, resources, bulk waste
Norgate (2001)	A comparative LCA of both hydrometallurgical and pyrometallurgical processes for the production of refined copper metal	Global warming potential, acidification, energy consumption
Norgate and Rankin (2000)	Life cycle assessment of refined metallic copper and nickel production, an investigation of pyrometallurgical and hydrometallurgical processing routes.	Global warming potential, acidification, energy consumption

Despite the benefits of LCA in the mining and mineral beneficiation industry, i.e. providing an assessment of environmental considerations during decision making, most of these studies only considered global impacts, i.e. climate change/global warming potential. However, very little has been mentioned about the waste handling aspect of the mining industry (Durucan et

al., 2006; Lesage, 2008) especially with regard to solid waste i.e. tailings, waste rocks and other residues. The quality of soils and water as a result of seepage from tailings impoundments which are generally considered as an emission to the environment are also not explicitly included in the LCA method (Stewart, 2001; Notten, 2001; Hansen, 2004; Stewart et al., 2004). These wastes often contain high concentrations of sulphide minerals (up to 30%), and as a result have the potential to contaminate local water sources and soils significantly (Harrison et al., 2010).

Only a few published studies have incorporated waste management and local waste-related impacts into LCA and LCI of mining operations (e.g. Stewart and Petrie, 1999; Durucan et al., 2006; Reid et al., 2009). Stewart and Petrie (1999) developed a system model of mining and mineral processing, which incorporated LCA methodology. The model reflected all environmental issues arising from resource extraction and minerals beneficiation including waste generation. The approach was proposed to assist operating companies in identifying their long-term liability associated with waste disposal and therefore guide the rehabilitation step. Durucan et al. (2006) developed a protocol model which incorporated a life cycle inventory database for the mining production, processing, waste handling and rehabilitation system within an LCA framework. The model enabled analysis of site-specific LCA impacts based on real data and its application was used on an open-pit bauxite mine in Hungary. However, these studies highlighted LCA deficiencies in terms of data availability and modelling capabilities. These limitations are addressed in the next subsection.

2.5.3 Limitations of LCA

The holistic nature of LCA has both major strengths and limitations, since analysing the life cycle of a product and/or a process has a wide scope (Guinée et al., 2001). Firstly, LCA is inherently a relative tool and does not quantify absolute impacts. The environmental impacts in LCA are characterised as potential impacts because of a lack of spatial and temporal dimensions in the analytical capabilities of the tool, and are always related to a defined functional unit (Guinée et al., 2001). Secondly, data quality availability is often quoted as a challenge. LCA is very dependent on the accuracy of its collected data and use of generic unit processes from LCA databases, in cases where there is no site specific data available. Thirdly, there is no single LCIA method used in conducting LCA studies. Available methods have varying scopes, different modelling principles as well as characterisation factors (Finnveden, 2009). Different LCIA methods can be used within one study. However, LCIA results would be expressed in different units of measure and are not directly comparable (e.g. Pizzol et al., 2011a; Pizzol et al., 2011b).This leads to LCA results being interpreted differently using different LCIA methods.

The limitations of LCA pertaining to the specific industry (chemical process industry and the mining and mineral beneficiation sector, particularly with regards to solid mineral waste) are addressed in the subsections below.

a) Chemical process industry

Generally there is a lack of LCI-data for the production of chemicals in the LCA databases and, due to confidentiality of information about a certain product, it is impossible to acquire data for chemical production processes directly from the producers (Geisler et al., 2004). This leads in choosing a chemical product that has similar properties as the one under study, frequently introducing uncertainties into the study (Von Bahr and Steen, 2004).

b) Mining and mineral beneficiation sector – solid mineral waste

LCA addresses emissions as steady- state and act over the life time of an operation, while in reality, in the case of solid mineral waste, there is often a time lag between the production of waste and its environmental impacts, and these environmental impacts associated with the waste emissions are known to be spatially dependent (Notten, 2001; Hansen, 2004; Reid et al., 2009). Relevant actual effects of solid mineral waste are largely ignored, in particular the salinisation and acidification of local waters. This makes LCA to be severely limited in its ability to incorporate solid waste impacts (Hansen, 2004). In addition to this, LCA results address global and regional environmental issues, local environmental impacts are not assessed to the same degree of accuracy as global and regional effects, because local effects depend on local conditions that LCIA methods are not able to take into account (Guinée et al., 2001).

The lack of comprehensive and reliable process inventory data to support environmental performance assessments and decision-making in the primary minerals sector has been highlighted in previous studies (Broadhurst et al., 2007; Norgate, 2001). This is a particular challenge in the case of high-volume solid wastes and processes for the management thereof, and is aggravated by the mineral ore and site-specific nature of many of the associated impacts (Hansen et al., 2008). In a recent study known to have specifically applied LCA in a comparison of tailings waste management options for the mitigation of acid rock drainage (ARD), deficiencies of LCA in terms of addressing impacts relating to the disposal and management of solid mineral waste were highlighted (Reid et al., 2009). These included lack of data to adequately describe background processes, particularly the production of raw materials in waste streams, and the absence of factors to characterise toxicity impacts of relevant water-related emissions e.g. calcium ion, chloride, silicon, sodium, ion and sulphate.

The study by Stewart and Petrie (1999) addressed in the previous subsection, highlighted the limitations of LCA in terms of assessing the long-term risks associated with different waste

disposal practices and still needed further development. The study by Durucan et al. (2006) highlighted the limitations of LCA with regards to characterisation of solid mineral waste impacts, in particular human and ecotoxicity. The characterisation of these impacts were not considered to be ideal due to the uncertainties of LCIA methodologies in addressing certain issues such as metals, persistence, speciation and bioavailability of elements after disposal.

Often, only the mass of solids waste produced in the mining and processing industry has been taken into account in LCA studies. Possible impacts associated with the generation of leachate and migrations of pollutants into the environment are completely ignored, with a few exceptions (Notten, 2001; Hansen, 2004). Solid wastes are often uncharacterised and the mechanisms controlling the rate and quality of leachate generation are poorly understood by LCIA models (Notten, 2001). Furthermore, emissions to water are less characterised by LCIA methods. In addition, toxicity (human and ecotoxicity) characterisation factors are not present for the most important major elements such as sulphates, chlorides, etc. These elements can have impacts on local water quality and its suitability for agriculture, domestic use, etc. Also, high levels of elements with low characterisation factors could be toxic to local aquatic organisms (Broadhurst and Petrie, 2010). LCA views salinity as an indicator that carries dissolved individual species such as metals. It therefore assesses the impacts of these substances and not the indicator itself (Notten, 2001).

There are also uncertainties and complex challenges regarding the assessment of toxicity of metals in LCIA methods (Pizzol et al., 2011a; Pizzol et al., 2011b). For example, the characterisation factor of metals in USEtox method are marked 'interim' This means that they may be used in LCA studies, but with great caution and under awareness of their large uncertainty to their interpretation as they are not recommended nor endorsed (Rosenbaum, 2008). High uncertainty is associated in the calculation of fate and effect factors of emitted substances through multi-media modelling, which is characterised by significant quantities of data. The factors characterising metals are overestimated because the transformation of metals into a less mobile and harmful form is not taken into account (Heijungs, 2004). This involves their chemistry, persistence in the environment, speciation, and bioavailability. For example, speciation of a metal is regulated by its chemistry and the surrounding environment (e.g. pH, redox potential, presence of ligands). These parameters are site-specific and multi-media models do not take them into account. Multi-media models are also limited in data availability of chemical and toxicological properties of certain substances, which often leads to the use of approximations or default values (Hansen, 2004). Therefore, this can greatly influence the total results of any LCA study regarding the toxicity assessment. Furthermore, the multi-media models were originally developed for organic chemicals and the approaches

used are not valid for inorganics (e.g. metals toxicity), without substantial uncertainties (Hansen, 2004; Hauschild, 2005; Finnveden et al., 2009; Pizzol et al., 2011b).

Another limitation of LCA with regard to solid waste management is the assessment of impacts associated with abiotic mineral resource depletion, which is a controversial topic (Klinglmair et al., 2014; Swart and Dewulf, 2013). This impact category is likely to be particularly challenging in the context of solid wastes, which represent a loss of resources due to non-utilisation rather than depletion. To date, this issue does not appear to have been addressed or even acknowledged.

2.6 Literature summary

The literature has reviewed and analysed information about xanthate salts in terms of their general production, environmental impacts and toxicity. Xanthate salts pose a risk of adverse health and environmental effects through exposure, particularly in production, transportation and use. It is considered to be a toxic chemical to aquatic life and its toxicity is related to its highly toxic by-products, particularly carbon disulphide, which is also a decomposition product of xanthate. Xanthate decomposition is mainly influenced by an increase in xanthate concentration (>10%), decrease in pH (<7) and increase in temperature (>20^{o}C). In aqueous solutions, xanthate dissociates into different pathways. Under acidic conditions, i.e. sulphidic tailings deposition, it decomposes to alkali metal hydroxide and xanthic acid, which decomposes further to carbon disulphide and alcohol. It also oxidise to dixathogen. Under alkaline conditions i.e. during sulphide ore flotation process, it decomposes to carbonate salts, carbon disulphide, trithiocarbonate salts and alcohol.

Due to the fact that carbon disulphide is a major ingredient in the production of xanthate as well as a decomposition product, its production and toxicity has been the subject of considerable research and invetigation. Carbon disulphide is highly volatile and flammable. It is toxic to both animals (LC_{50} of 25 g/m^3 for two hours for rats) and humans (320-390 ppm for several hours) upon exposure. Carbon disulphide has previously been produced using charcoal as a raw material, due to its demand in the late nineteenth century, a more efficient production process was developed which involved the use of natural gas as a feedstock. This new process offers a number of operating advantages compared to the old process, i.e. operating at lower temperatures. So far there has been no attempt to quantify the environmental benefits of this process over the old process and its effects on the environmental footprint of xanthate.

Besides their common use as a collector in the primary processing of metallic sulphides ore, xanthate salts have also recently been investigated for the pre-disposal removal of sulphide

minerals from mine wastes, by means of desulphurisation flotation, with a view to mitigating acid rock drainage (ARD). ARD is generated when the sulphide minerals in mine wastes are exposed to air, water and naturally occurring iron and sulphur oxidising bacteria, during disposal. Acid rock drainage is characterised by acidic pH values (<6), high salinity and elevated metal concentrations, and is a serious environmental problem in the mining industry. The contaminated leachate has adverse environmental effects to surroundings areas, particularly on water quality and water sources (ground and surface) leading to serious human and ecotoxicity effects associated with metal contamination.

Studies reported in the literature have demonstrated that the use of xanthate salts in the conceptual desulphurisation flotation process can greatly reduce ARD risk by reducing the sulphur content in sulphide tailings. It is also considered to be an economically viable method as compared to other ARD mitigation methods. However, to date, studies of the environmental performance of the desulphurisation flotation process have been limited with little consideration being given to the impacts associated with background processes, additional resource utilisation and/or recovery, and reduced waste burden.

LCA is an environmental assessment tool that can be used to determine life cycle impacts associated with both products and processes. A number of life cycle impact assessment (LCIA) methods have been developed over the past 20 years. One of the current state-of-the-art methods in LCIA is that of ReCiPe. This method was developed on the improvement of other methods and combines both midpoint and endpoint levels. Usetox method has also been developed through a process of harmonisation of other existing models and forms a basis for future global recommendations of characterisation of human and ecotoxicity impacts. However, LCA method has its limitations. Generally, environmental impacts are characterised as potential impacts because of a lack of spatial and temporal dimensions, data quality availability is often a challenge as LCA is very depended on the accuracy of its collected data and different LCIA methods can be used to perform a specific study, but can result in different interpretation of results as LCIA methods vary, particularly in characterisation factors of emissions. LCA is severely limited in its ability to incorporate solid mineral waste impacts, particularly salinity and acidification of local waters. Dissolved metals in solid mineral waste are considered to have high uncertainty in LCIA methods due to the uncertainty of multimedia modelling. These models do not take into account relevant information of metals e.g. their speciation.

2.7 Research objectives

As highlighted in Chapter 1, this project aims to investigate the environmental performance of xanthate production and its application in the mitigation of ARD, specifically this project will use the life cycle assessment (LCA) approach to identify and compare:

(i) The environmental impacts of the current and previous carbon disulphide production processes, as well as the subsequent effects of such on xanthate production.
(ii) The environmental benefits and/or impacts of the desulphurisation flotation and conventional base metal tailings treatment and management processes, insofar as xanthate is used as a sulphide collector in the desulphurisation process.

This project aims to address the following research questions:

(i) How does the environmental performance of the new facility for CS_2 production compare with that of the previous process?
(ii) What effect has the new CS_2 production process had on the environmental performance of subsequent xanthate production?
(iii) How does the environmental performance of the desulphurisation flotation process for the pre-disposal treatment of sulphide tailings compare with the conventional management approach?
(iv) What are the key environmental issues and challenges associated with the proposed desulphurisation flotation process for the mitigation of ARD?
(v) What are the strengths and limitations of current LCA tools in terms of reliably quantifying the systems under investigation in this study?

Chapter 3

METHODOLOGY

In order to meet the study objectives and address the research questions, the study has been divided into a two step process: LCA of xanthate production (LCA 1) and LCA of ARD mitigation (LCA 2). These are performed according to the four steps of LCA framework provided by the ISO standards, which are: goal and scope, life cycle inventory (LCI), life cycle impact assessment (LCIA) and Interpretation. These methodological steps are discussed in subsection 3.1 (LCA 1) and subsection 3.2 (LCA 2). Simapro software package (version 7.3.3) developed by PRé Consultants in the Netherlands (PRé Consultants, 2012) was used to organise LCI data and quantitatively characterise it according to the type of environmental impacts selected.

3.1 Life cycle assessment study 1: Xanthate production

3.1.1 Goal and scope definition

The goal of this study was to: *Use life cycle assessment (LCA) to identify and compare the environmental impacts of the current and previous carbon disulphide production process, as well as the subsequent effects of such on xanthate production at Senmin®'s Sasolburg production site.*

The system boundary is consistent with a cradle-to-gate approach, i.e. from the raw extraction of materials to production of the final product (Figure 10). The function of the process system compared is the production of xanthate salts from carbon disulphide, noting that the difference between the old and new production processes is the intermediate carbon disulphide product. The functional unit is 1 tonne of carbon disulphide produced. This reference flow is then used to determine the environmental impacts in the production of xanthate.

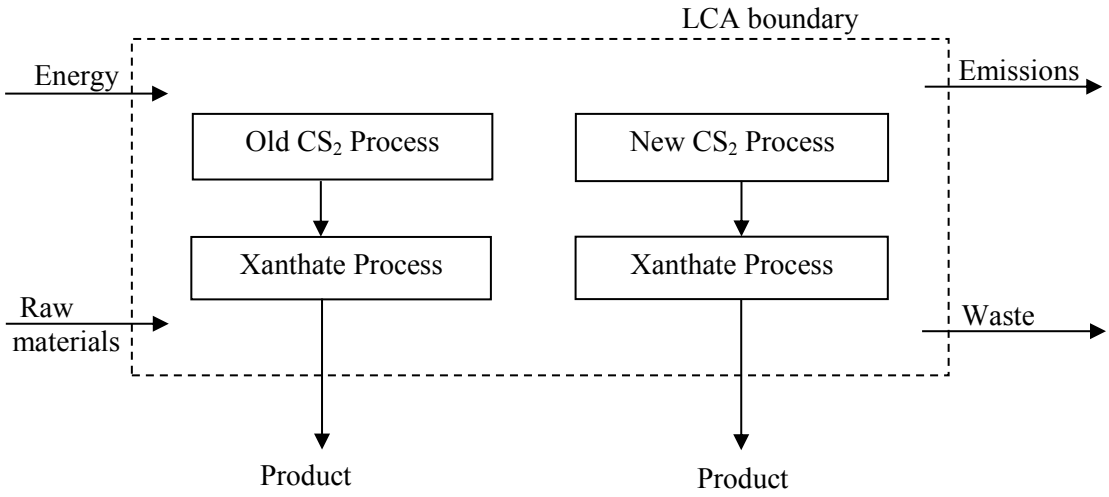


Figure 10: Overall LCA boundary of xanthate production

Impact categories were selected on the basis of their relevance to the production of carbon disulphide intermediate and final xanthate products, focussing mainly on the following impact categories:

- *Climate change* – Global warming due to greenhouse gas emissions in the atmosphere
- *Fossil fuel depletion* – Non-renewable resource depletion due to extraction and consumption of fossil fuels
- *Acidification* – Change of acidity in the soil by acid rain due to gaseous SO_2 emissions
- *Human toxicity* – Effects of toxic substances on human health.
- *Ecotoxicity* – Damage to ecosystem quality as a result of emission of toxic substances to air, soil and water.

3.1.2 Inventory analysis

Foreground data was obtained for annual production sheets and personal communication with relevant Senmin® representatives. Ecoinvent (version 2.2) database found in SimaPro software was used to obtain data for background processes i.e. production of energy and input materials. Current average technologies were used and information pertaining to electricity production mix for South Africa was substituted to reflect local conditions.

3.1.3 Impact assessment

Using SimaPro software, the ReCiPe midpoint methodology was used to interpret the collected data (foreground and background) into meaningful preselected impact categories as defined in the goal and scope stage. A potential improvement option for the new carbon disulphide was analysed.

3.1.4 Interpretation

Further interpretation of results was carried out to determine the relative contributions of processes to the impact categories, and to explore opportunities for further improving the environmental performance.

3.2 Life cycle assessment study 2: Xanthate use in the tailings desulphurisation flotation

3.2.1 Goal and scope definition

The goal of the second LCA methodology was to: *Assess and compare the environmental benefits and/or impacts of the desulphurisation flotation and conventional base metal tailings treatment and management processes, insofar as xanthate is used as a sulphide collector in the desulphurisation process.*

This study developed two scenarios for the treatment of tailings slurry stream generated during the milling and flotation of base metal sulphide ores (Figure 11). The first scenario, referred to as the "base case scenario" involves conventional dewatering of the tailings in a cylindrical continuous thickener, to produce an underflow stream which is discharged to a tailings impoundment. After solids settling, the decant water is recycled, together with the thickener overflow, to the main processing plant. Seepage contains residual flotation chemicals, as well as acid, salts and metals mobilised through the reaction of residual sulphides and acid neutralising carbonate minerals in the tailings during disposal. In this way, the deposit is considered as a unit operation generating its own emissions to air (water vapour and CS_2 from xanthate decomposition) and water (seepage) and having a land requirement (unreacted tailings), as well as a product output in the form of recovered water.

The second treatment scenario, referred to as the "desulphurisation flotation scenario", entails the tailings slurry being subjected to desulphurisation flotation, using a xanthate collector, and the desulphurised tailings fraction subsequently subjected to dewatering and disposal as in the base case scenario. The flotation concentrate stream is dewatered by means of filtration to produce a sulphide-rich by-product which can be recycled to the primary metal extraction circuit for further processing to produce acid and/or recover base metal values. However, this is not included in the LCA scope. In order to fully analyse the potential environmental impacts of the desulphurisation process and its effect using xanthate, two sub-scenarios were developed for the behaviour and deportment of xanthate during the disposal of the desulphurised tailings. These are referred to as scenario A (deportment of soluble xanthate to tailings dam seepage without decomposition) and scenario B (decomposition of soluble

xanthate to carbon disulphide, alcohol and sodium hydroxide under disposal conditions, in accordance with reactions 6 and 7 in subsection 2.1.1, Chapter 2).

The scope of this study covers a gate-to-grave approach. It takes into account data from the modelled xanthate (via the new carbon disulphide production process) in LCA 1 study as input material to the desulphurisation process. The environmental impacts of the background mining and mineral processing operations have not been included, as these are common to both tailings management options being compared. However, consideration is given to the physio-chemical changes that the tailings undergo during disposal. In this way the tailings deposit is considered as a 'unit operation', putting the leachate generated on a par with process emissions.

The function of this study is to assess mine tailings management options (based on data found in literature). Therefore the functional unit is defined as 'the management of 100 tonnes of dry tailings' that are acid generating.

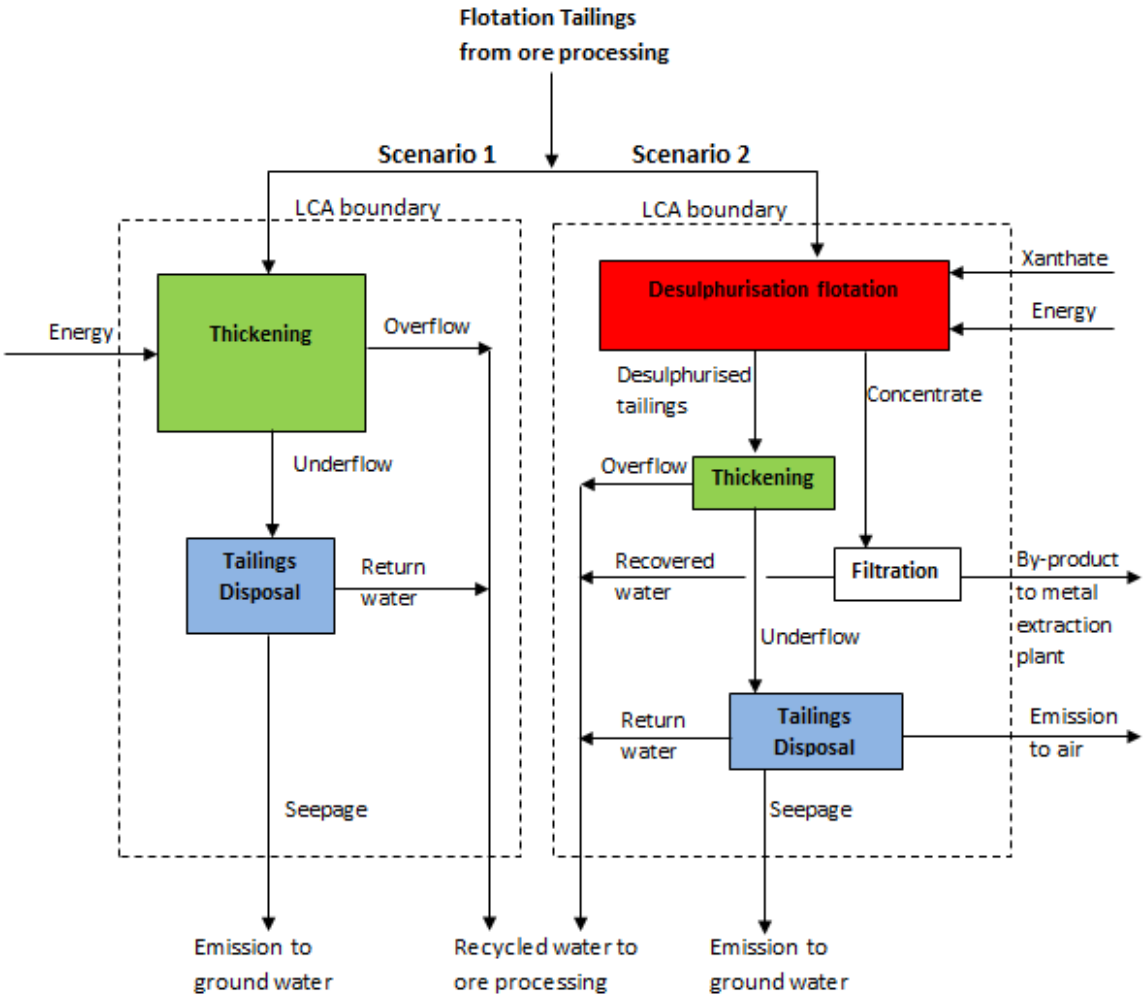


Figure 11: Overall LCA boundary of the desulphurisation flotation process and the conventional process treatment scenarios.

The following impact categories that are relevant to the use of xanthate in the desulphurisation flotation process have been selected:

- *Climate change* – Global warming due to greenhouse gas emissions in the atmosphere
- *Fossil fuel depletion* – Non-renewable resource depletion due to extraction and consumption of fossil fuels
- *Acidification* – Change of acidity in the soil by acid rains due to gaseous SO_2 emissions
- *Natural land transformation* – The amount of natural land transformed and occupied for a certain time
- *Urban land occupation* – The amount of urban land occupied for a certain time.
- *Human toxicit y*– Effects of toxic substances on the human health
- *Ecotoxicity* – Damage to ecosystem quality as a result of emissions of toxic substances to air, soil and water.

3.2.2 Inventory analysis

The overall LCA system boundary for both desulphurisation flotation and base case scenario is given and explained in more detail in Chapter 5. Life cycle inventory modelling for each of the systems was conducted using the Simapro software (version 7.3.3) at the selected reference flow rate (100 tonnes of dry tailings). The system boundaries included background processes, namely electricity production (mix for South Africa was used to reflect local conditions) and xanthate production (derived from the modelled xanthate in LCA 1 study)

Parameters for the foreground systems were derived from a combination of literature information, in-house knowledge and mass balance calculations. The composition of the feed tailings, xanthate dosage and desulphurisation flotation output was obtained from a base metal case study conducted by Benzaazoua and Kongolo (2003).

3.2.3 Impact assessment

The life cycle impact assessment (LCIA) stage involved the relative interpretation of the collected inventory data into the preselected impact categories using two methods. ReCiPe method was used to assess climate change, fossil depletion, terrestrial acidification, natural land transformation and urban land occupation impacts. Although generally considered to be the state-of-the-art in terms of LCIA modelling, the ReCiPe method does not include factors to characterise xanthate toxicity. Therefore, USEtox method was used as an additional method to assess human and ecotoxicity impacts.

3.2.4 Interpretation

This stage involved a sensitivity analysis. This analysis determined the sensitivity of selected impact categories related to key parameters. Parameters analysed were 1) impact of energy consumption on climate change, fossil depletion and terrestrial acidification, 2) impact of zinc feed concentration and mobility on toxicity, 3) impact of copper feed concentration on toxicity. The limitations of the study included input data quality (in terms of both availability and certainty), impact categories considered, as well as the LCIA modelling capabilities.

Chapter 4

LIFE CYCLE ASSESSMENT OF XANTHATE PRODUCTION

The goal of the first life cycle assessment study is to identify and compare the environmental impacts of the current and previous carbon disulphide production process, as well as the subsequent effects of such on xanthate production at Semin®'s Sasolburg production site. This chapter of the dissertation presents and discusses the results of this life cycle assessment study, and includes a description of the production processes, the life cycle inventory, impact assessment modelling and interpretation of model outcomes.

4.1 Description of the production processes

This section describes the old and new processes for the production of carbon disulphide (subsections 4.1.1 and 4.1.2 respectively), and the xanthate production process (subsection 4.1.3)

4.1.1 Old CS_2 production process

The old CS_2 plant can be divided into three main unit operations; charcoal preparation, sulphur preparation and CS_2 production. These unit operations are described in further detail in the subsections below. The process flow diagram with key inputs and outputs is presented in Figure 12.

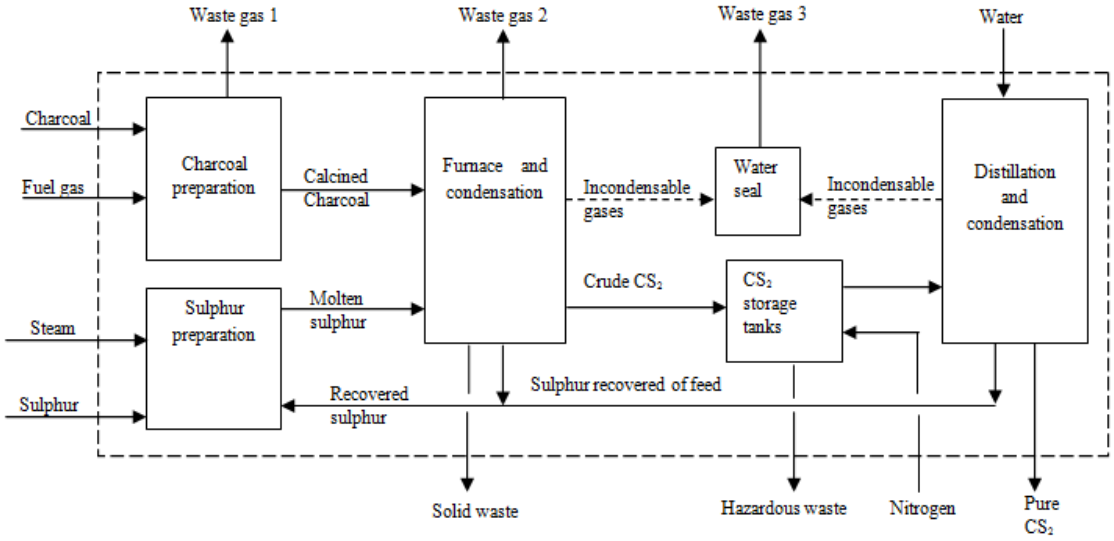


Figure 12: Process flow diagram for the old CS_2 production system

Charcoal preparation

Charcoal is procured from a vendor in Mpumalanga province (distance of 500km to site) and stored in bags or in bulk at the plant. It is prepared by heating in a calciner to reduce its content of ash, moisture and volatiles, namely absorbed hydrogen and oxygen compounds. These impurities are undesirable because they form sulphur compounds, mainly hydrogen sulphide, and contributed to sulphur losses and plant inefficiency. The charcoal is heated to approximately 700-900^{o}C, using heat from a fuel gas burner. The hot gases, mainly carbon dioxide, from the burner, pass through the calciner and are exhausted together with the moisture and volatiles driven out of the heated charcoal (waste gas 1, Figure 12). After calcination, the charcoal is placed in hoppers before being transported by means of a forklift truck to the combustion furnace.

Sulphur preparation

Sulphur is procured in liquid form from a nearby refinery and is placed into a sulphur pit, where it is kept hot by steam heated coils. From the pit, the liquid sulphur is pumped in jacketed steam heated pipes to the furnace in metered quantities.

CS_2 production

The CS_2 production process can be subdivided into four operational stages; furnace combustion, gas separation and condensation, distillation and CS_2 storage.

- ***Furnace combustion***

The combustion reaction in the furnace is represented by Equation 2 in subsection 1.1.1, Chapter 1:

$C + S_2 \rightarrow CS_2$

The charcoal is introduced to the furnace top at timed intervals through gas-tight feeders. A continuous metered flow of molten sulphur is distributed to the furnace at several points. The amount of sulphur fed into the furnace depends on the desired production. As a general rule, approximately one tonne of sulphur is fed into the reactor for each tonne of carbon disulphide produced. This approximation takes into account the recycled sulphur stream, and equates to a conversion efficiency of approximately 85%. The heat required for bringing the raw materials to a reaction temperature between 800 and 1000^{o}C is generated by electrical resistance in the charcoal, which functions as a conductor between two furnace electrodes. The power to the electrodes is regulated by variable voltage control of a single phase transformer. The sulphur is vaporised and reacted with the charcoal to form carbon disulphide, in accordance with Equation 2. Volatile matter and moisture contained in the charcoal react with the sulphur to form various gaseous by-products mainly hydrogen sulphide (H_2S). Other gases formed are nitrogen (N_2), carbon dioxide (CO_2), carbon monoxide (CO), and carbon oxysulphide (COS).

A safety disc is installed in the gas outlet of the furnace. When pressure in the furnace is too high, this safety disc is blown off. When this happened, product and by-product gases from the furnace are flared before being emitted to the atmosphere mainly as SO_2 (waste gas 2, Figure 13). Accumulated ash from the charcoal and from the sulphur is removed as solid waste, together with the unreacted charcoal, on a regular basis.

- ***Separation and condensation***

Product gas and by-product gases from the furnace pass through a charcoal separator. Most of the fines and particulate matter in the gas stream are separated and collected in the bottom of the charcoal separator, and the rejected material recycled to the furnace. The gases pass through a steam - heated sulphur separator. Most of the unreacted sulphur collected in the separator and overflow continue into a sulphur measuring tank. The recovered sulphur amounts to 8-12 % of the feed sulphur and is recycled back to the sulphur pit. The gases are then fed to a condenser unit. From the condenser, crude liquid carbon disulphide is sent to storage tanks. Uncondensed gases, consisting essentially of H2S, CO, H2, N2, COS, CO2 and residual CS2, pass through a water seal and are flared before being releasing as SO2 into the

atmosphere (waste gas 3, Figure 12). These gases are not recovered, as a relatively small quantity is produced.

- ***Distillation***

The crude carbon disulphide from the furnace condensers contains some dissolved sulphur and hydrogen sulphide as impurities. To remove these impurities and to bring the product up to the desired final quality, the crude carbon disulphide is passed continuously through two distillation columns, one for sulphur removal and the other for separation of hydrogen sulphide. The purified carbon disulphide is then sent to storage tanks, while the recovered sulphur is returned to the sulphur preparation area.

- ***Product storage***

Crude and pure carbon disulphide is stored in tanks, which are submerged in a water filled pit for safety reasons. The tank space above the carbon disulphide is filled with either water or nitrogen to prevent air entering. Occasionally these tanks are cleaned. CS_2 sludge is scrapped out as hazardous waste, which is taken to a hazardous waste treatment plant.

4.1.2 New CS_2 production process

The new CS_2 plant consists of four main unit operations: sulphur preparation, heating and reaction, sulphur separation and sulphur recovery. The process units are described in detail in the subsections below. Figure 13 shows the process flow diagram and identifies the input and output materials.

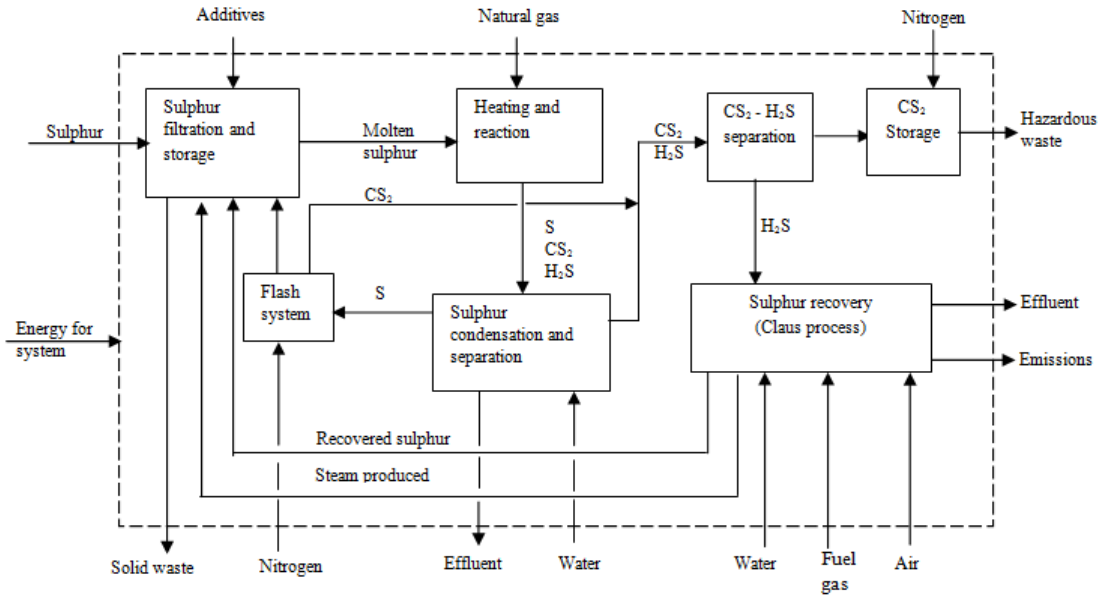


Figure 13: Process flow diagram for the new CS_2 production system

Sulphur filtration and storage

As in the case of the old CS_2 process, molten sulphur is received from the nearby refinery and is stored in a sulphur accumulation pit. From there, the sulphur is transferred to a sulphur mixing pit. Before being fed to the furnace, it is filtered to remove impurities, which, if not removed, would cause obstruction and other processing difficulties. Additives (lime, filtration aid and activated clay) are added in the sulphur mixing pit before the filtration process. The filtered sulphur is collected in a sulphur storage pit and the residues are collected separately as solid waste for disposal.

Heating and reaction

Methane reacts in a reaction coil with diatomic sulphur according to the following endothermic reaction as previously seen in Equation 3, subsection 1.1.1, Chapter 1.

$CH_4 + 4S \rightarrow CS_2 + 2H_2S$

The reaction takes place at temperatures between 600-630^oC, with heat provided by gas fired heaters. Excess sulphur (10%) is used to ensure a maximum conversion of CH_4. The plant has been designed to achieve a 96% conversion of methane. The reaction gases consist mainly of carbon disulphide and hydrogen sulphide, with some unreacted sulphur.

Sulphur separation

Unreacted sulphur is removed from the reaction gases in a sulphur condenser. The condensed sulphur contains CS_2 and some dissolved H_2S and is therefore sent to a flash system, where atmospheric conditions vaporise the CS_2, separating it from sulphur that is recycled to the filtration stage to remove impurities. The vaporised CS_2 from the sulphur flash system is first condensed and recycled to the CS_2-H_2S separation unit, together with the CS_2 from the distillation column. Boiler blow-down from steam boilers is collected as effluent. The gases at the outlet of the condenser comprise mainly CS_2 and H_2S.

H_2S-CS_2 separation

Carbon disulphide is separated from hydrogen sulphide by absorption, and subsequently stripped and sent to a distillation column to remove small amounts of impurities. Overhead condensers are used on the distillation column where partial condensation of H_2S occurs, serving as a reflux. Off-gas from the carbon disulphide absorber, which comprises H_2S gas that is practically free of CS_2, flows to a sulphur recovery unit (Claus process). Carbon disulphide, retrieved at the bottom of the column, is free of H_2S which is cooled and sent to

storage tanks, where it is stored under water prior to being distributed to the xanthate production plant.

Sulphur recovery (Claus process)

The sulphur contained in the H_2S gas stream is recovered using the conventional Claus process, as previously mentioned in the literature review, (subsection 2.2.1). In this process H_2S is converted to elemental sulphur in two stages, represented by the reactions in Equations 11 and 12

$$2H_2S + 3O_2 \rightarrow 2SO_2 + 2H_2O \qquad \text{Equation 17}$$

$$SO_2 + 2H_2S \rightarrow 3S + 2H_2O \qquad \text{Equation 18}$$

In the first reaction step, H_2S gas passes through a thermal reactor where it is combusted with air to form sulphur dioxide (Equation 11). The process gas is cooled in a boiler down to a temperature of 260^{o}C. The process heat from this reaction as well as the condensation heat from the boiler is used to produce medium pressure steam that gets used in other processes in the plant. The cooled sulphur dioxide gas subsequent gas (sulphur dioxide) then passes through three catalytic stages where it is reacted with residual hydrogen sulphide on a catalyst to form sulphur (Equation 12). The three catalytic stages are operated at different temperatures, which decrease from the first stage to the last stage. Downstream of each catalytic reactor is a condenser where the sulphur is removed from the gas stream. The sulphur product is recycled to the sulphur feeding tank for reaction in the furnace. Heat from the condensers is used to produce low pressure steam that is used in sulphur filtration and storage stage i.e. for jacketed sulphur pipelines, coils, pumps and vessels. Boiler blow-down from steam boilers is collected as effluent. The gas (tail gas) emerging from the last catalytic reactor flows to a thermal incinerator, where any unreacted hydrogen sulphide is converted to sulphur dioxide at high temperature. The incinerator is fired by natural gas fired heaters. The gaseous emissions, comprising mainly SO_2 and CO_2, are then discharged to the atmosphere through a stack.

CS_2 storage

Product carbon disulphide is stored in tanks. The tank space above the carbon disulphide is filled with nitrogen to prevent air entering. Once in a while these tanks are cleaned. CS_2 sludge is scrapped out as hazardous waste.

Flare system

As a safety measure, there are points throughout the CS_2 plant where S, CH_4, H_2S or CS_2 may be released from the process system through pressure relief valves. These materials are toxic and flammable. They cannot be safely vented within the operating area and are collected and rendered less noxious by burning in a flare. Continuous nitrogen purge flow to the flare stack is used for sweeping air that may enter the stack as a result of diffusion. Any back flash is prevented by flare design and seals.

4.1.3 Xanthate production process

Senmin® produces a complete range of xanthate products including ethyl, isobutyl, propyl and pentyl xanthate. These are supplied in three different forms; powder, pellets and liquid. The process of producing solid xanthate (powder and pellet) involves three similar and interchangeable steps: reaction, drying and solids handling, which are performed in a single plant. Liquid xanthate is produced in a separate plant where the drying and solids handling section is not involved. The name and type of a xanthate is derived from the alkali and alcohol from which it is manufactured, i.e. SEX (sodium ethyl xanthate) is manufactured from sodium hydroxide and ethyl alcohol. As SEX in a liquid form is the major product manufactured at Senmin®, the life cycle assessment study was performed for this product only. Figure 14 depicts the process flow diagram of sodium ethyl xanthate, identifying the input and output materials.

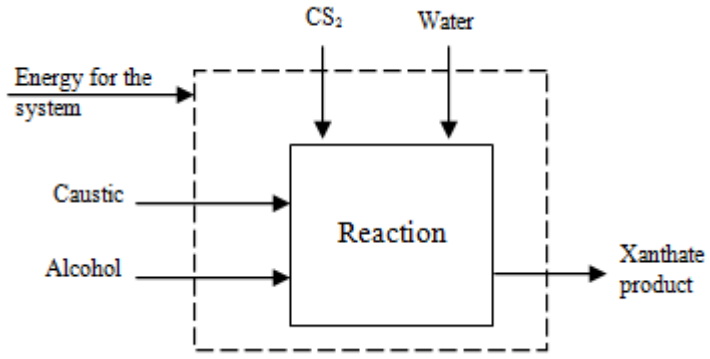


Figure 14: Liquid sodium ethyl xanthate production process

Production of salts is essentially carried out in a batch system. Xanthate salts are formed by the reaction of carbon disulphide with alcohol and caustic (either sodium hydroxide or potassium hydroxide), as previously represented by Equation 1 (subsection 1.1.1, Chapter 1).

$$ROH + CS_2 + MOH \rightarrow ROCS_2M + H_2O$$

The reaction is usually carried out in two steps: the alcoholation reaction, whereby the alcohol reacts with caustic to form sodium or potassium alcoholate and water; and the xanthation reaction, where the alcoholate formed is combined with carbon disulphide to form xanthate. Precooled alcohol is added to the reactor, in excess of that required for reaction. While the alcohol is recirculating, flake caustic is slowly fed into the reactor. Heat is released during the alcoholate reaction, but the final batch temperature is kept low by continuous flow of refrigerant through the reactor jacket. When the addition of caustic is complete, carbon disulphide is fed to the reactor under continued refrigeration. The CS_2 feed is regulated to maintain a low reactor batch temperature. When sufficient CS_2 has been added, the CS_2 flow shuts off automatically. After the reaction step the xanthate is diluted with water to 40% prior to bulk storage tanks. Emissions from the xanthate plant are reported to be negligible as neither the solid nor the liquid plants generate solid or liquid effluents. All non-product outputs are returned to the process for conversion to xanthate.

4.2 Life Cycle Inventory

The purpose of the studied inventory is to accurately characterise inputs (raw materials input, process chemicals, energy and water consumption) and outputs (emissions and wastes) within the defined system boundary, beginning from the extraction of raw material and ending with the final product. This section describes the system boundaries and relevant parameters for the production of carbon disulphide (subsection 4.2.1) and xanthate (subsection 4.2.2).

4.2.1 Carbon disulphide production system

The overall system boundaries, depicting both the background and foreground sub-systems for the old and new carbon disulphide processes, are presented in Figures 15 and 16 (on page 60-61) respectively. In both cases, data for the foreground system is based on the actual operation of this system during one year and is thus the primary data. The background system comprises the off-site processes which supply the inputs to, and/or process the outputs from, the foreground system.

Foreground datasets

- **Old CS_2 process**

Input and output data for the old CS_2 process was collected from the year 2009 annual production and environmental records, and a weighted average was calculated from the annual data. The raw data is presented in Appendix B, Table B1. From the weighted average the inputs and outputs are calculated based on 1 tonne of CS_2 produced, which is the

reference flow. In cases where plant data was not available due to confidentiality or other reasons, parameters were derived from mass balance calculations. Detailed mass balances calculations and assumptions are provided in Appendix B, Table B3. Parameters for the old carbon disulphide production process (foreground system) is summarised in Table 9 (page 58).

Carbon and sulphur mass balances (Table 6) indicate recoveries of 97% and 99% respectively. The 3% carbon unaccounted for may be due to an overestimation of the amount of feed charcoal and/or an underestimation of carbon emissions. The calculated input amounts for carbon and sulphur are consistent with literature data. Raw material usages per tonne of CS_2 product are approximately 220 – 250 tonnes charcoal and 920 – 950 tonnes sulphur (including recycle) (Smith and Timmerman, 2000)

Table 6: Carbon and sulphur mass balance arising from the production of 1 tonne CS_2 via the old process

Sources	Total inputs (kg/tonne CS_2 produced)	Total outputs (kg/tonne CS_2 produced)	Losses (kg/tonne CS_2 produced)	Recovery (%)
Carbon Species				
Charcoal feed	185.6	-		
Fuel gas (Methane (CH4)	26.3	-		
Solid waste (unreacted charcoal)	-	17		
CO_2 in waste gas	-	29.4		
CS_2 product	-	157.8		
Hazardous waste (CS_2)	-	1.3		
Total Carbon	**211.9**	**205.5**	**6.4**	**97**
Sulphur Species				
Feed sulphur	891.8	-		
Sulphur in product	-	10.2		
H_2S in product	-	3.84		
SO_2 in waste gas	-	16.9		
CS_2 product	-	842.3		
Hazardous waste (CS_2)	-	7		
Total Sulphur	**891.8**	**880.21**	**10.6**	**99**

- **New CS_2 process**

Input and output data for the new CS_2 process was collected from the year 2011 annual production and environmental records and a weighted average was calculated from the annual data. Raw data is presented in Appendix C, Table C1. From the weighted average, the inputs and outputs are calculated based on 1 tonne of CS_2 produced which is the reference flow. In

cases where plant data was not available due to confidentiality or other reasons, parameters were derived from mass balance calculations. Detailed mass balance calculations and assumptions are provided in Appendix C, Table C3. Parameters for the new carbon disulphide production process (foreground system) is summarised in Table 10 (Page 59).

Carbon and sulphur mass balances (Table 7) indicate recoveries of 95% and 99% respectively. The 5% carbon unaccounted for may be due to an overestimation of the amount of feed natural gas and/or an underestimation of carbon emissions. The calculated input amount for the sulphur is consistent with literature data. Raw material usage per tonne of CS_2 product is approximately 860 - 920 tonnes sulphur (including Claus sulphur recovery efficiency) (Smith and Timmerman, 2000)

Table 7: Carbon and sulphur mass balance arising from the production of 1 tonne CS_2 via the new process

Source	**Total inputs (kg/tonne CS_2 produced)**	**Total outputs (kg/tonne CS_2 produced)**	**Loses(kg/ tonne CS_2 produced)**	**Recovery (%)**
Carbon species				
Methane (CH_4)	164.4	-		
Fuel gas	105.6	-		
CO_2 in waste gas	-	98.9		
CS_2 product	-	157.8		
Hazardous waste (CS_2)	-	0.4		
Total Carbon	**270**	**257**	**12.9**	**95**
Sulphur species				
Sulphur feed	877.37	-		
SO_2 in waste gas	-	20.3		
Solid waste (sulphur)	-	1.1		
CS_2 product	-	842.3		
Hazardous waste (98% CS_2)	-	2		
Total Sulphur	**877.37**	**865.6**	**11.7**	**99**

Foreground analysis of the compared old and new CS_2 process parameters

Table 8 summarises the foreground parameters derived for the old and new CS_2 process on the basis of the reference flow (1 tonne of carbon disulphide produced).

Table 8: Summary of key foreground parameters for the production of 1 tonne CS_2 via the old and new process

Description			Unit	Flows per tonne of CS_2 produced	
				New CS_2 (2011)	Old CS_2 (2009)
Inputs	**Energy**	Electricity	GJ	0.8	5.7
		Steam	GJ	6.5	12.7
		Natural gas	GJ	7.5	2.0
		Total energy	GJ	14.9	20.0
	Materials	Water	m^3	1.4	4.3
		Nitrogen	m^3	13.05	49.6
		Carbon source material	kg	224.0[1]	224.0[2]
		Sulphur	kg	881.8	898.6
Outputs	**Waste and emissions**	Effluent	m^3	0.6	0.3
		Solid waste	kg	1.9	24.6
		Hazardous waste	kg	2.4	8.5
		SO_2	kg	40.5	33.8
		CO_2	kg	362.4	107.93
	Product	CS_2	kg	1000	1000

[1]natural gas; [2]charcoal

The compared results show that the new process utilises 25% less energy than the old process, with significant reductions in electricity (86% reduction) and steam (49% reduction) consumption. The new process also consumes a lot less water (67% less) but results in higher effluent (50% more) than the old process. It also produces significantly less solid waste (92% reduction) and hazardous waste (72% reduction). However, it results in slightly higher SO_2 emissions (17% more) than the old process, and significantly higher CO_2 emissions (70% more), which can in turn be attributed to the higher utilisation of natural gas for energy. The calculated raw materials used for both processes have the same quantity in terms of the carbon source material and slightly different sulphur quantity which is due to the different plant conversion of each plant.

Table 9:Foreground process data arising from the production of 1 tonne CS_2 via the old process

Description			Units	Annual (2009)	Monthly average	Unit per tonne of CS_2	Data source	Comments
Inputs	Energy	Electricity	GJ	42898.82	3574.90	5.66	Production sheet	Electricity from the grid was used for furnace operation
		Steam	GJ	96474.24	8039.52	12.73	Production sheet	Steam was used for blanketing of sulphur pits and pipeline,
		Fuel gas	GJ	14752.84	1229.40	1.95	Production sheet	Fuel gas was used as energy for the calcination process
		Total energy	GJ	154125.90	12843.82	20.34	Production sheet	Total energy used (electricity, steam and fuel gas)
	Materials	Water	m^3	32413	2701.08	4.28	Production sheet	Water was used for cooling purposes
		Nitrogen	m^3	375650	31304.17	49.57	Production sheet	Nitrogen was used for purging of plant equipment
		Charcoal	kg	-	-	223.6	Stoichiometric cal.	Charcoal was used as a raw material and is calculated based on stoichiometric balance, assuming 85% conversion.
		Sulphur	kg	-	-	898.56	Stoichiometric cal.	Sulphur fresh feed (total flowrate) was used as raw material and is calculated based on stoichiometric balance, excluding recycle stream.
Outputs	Waste	Effluent	m^3	4641.01	386.75	0.34	Production sheet	Effluent from cooling water blow downs was taken to an off-site waste treatment plant.
		Solid waste	kg	340254.26	28354.52	24.61	Production sheet	Solid waste, mostly ash from the furnace was taken to an off-site solid waste treatment plant.
		Hazardous waste	kg	116900	9741.67	8.45	Production sheet	Hazardous waste which was sludge collected from CS_2 storage tanks, was taken to a hazardous waste treatment plant.
	Emissions	SO_2	kg	256044	21337	33.8	Production sheet	Total SO_2 emitted to the atmosphere by the plant due to bursting of safety disc (waste gas 2 and 3, Figure 13)
		CO_2	kg	-	-	107.9	Stoichiometric cal.	Calculated based on combustion of fuel gas and bursting of safety disc.
		Volatiles	kg	-	-	12.3	Calculated	Volatiles are emitted during calcination process and originate from the impurities of coal.
	Product	CS_2	tonne	7578.90	631.57	1	Production sheet	Produced product, stored, and sent to xanthate process plant.

Table 10: Foreground process data arising from the production of 1 tonne CS_2 via the new process

Description			Unit	Annual (2011)	Monthly average	Unit per tonne of CS_2 produced	Data source	Comments
Inputs	Energy	Electricity	GJ	9618.02	801.50	0.81	Production sheet	Electricity from the grid is used for plant equipment operations
		Steam, net	GJ	77242.12	6436.84	6.54	Production sheet	Less steam was produced by process as opposed to design specs. Therefore system used outsourced steam for blanketing of sulphur pits and pipeline,
		Fuel gas	GJ	88685.7	7390.48	7.51	Production sheet	Fuel gas from pipeline is used to assist for incinerator or flare in the sulphur recovery unit
		Total energy	GJ	204700.92	17058.41	14.86	Production sheet	Total energy used (electricity, steam and fuel gas)
	Materials	Water net	m3	16286.65	1357.22	1.38	Production sheet	Water is used for cooling purposes
		Nitrogen	m3	154088.1	12840.68	13.05	Production sheet	Nitrogen is used for purging of plant equipment
		Natural gas	kg	2645841	220486.75	224.02	Production sheet	Natural gas, mostly methane is used as a raw material
		Sulphur	kg	-	-	881.78	Calculated	Sulphur fresh feed is used as raw material and is calculated based on stoichiometric balance, excluding recycle stream
Outputs	Waste	Effluent	m^3	6641	553.42	0.56	Production sheet	Effluent from cooling water blow downs is taken to an off-site waste treatment plant.
		Solid waste	kg	21999.50	1833.29	1.86	Production sheet	Solid waste from sulphur filtration is taken to an off-site solid waste treatment plant.
		Hazardous waste	kg	28350	2362.50	2.40	Production sheet	Hazardous waste which is sludge collected from CS_2 storage tanks, is taken to an off-site hazardous waste treatment plant.
	Emissions	SO_2	kg	478331	39860.92	40.5	Production sheet	SO_2 emitted to the atmosphere, due to flaring of tail gas from sulphur recovery unit.
		CO_2	kg	4279673	356639.42	362.36	Production sheet	CO_2 emitted to the atmosphere, due to flaring of tail gas from sulphur recovery unit.
	Product	CS_2	tonne	11810.68	984.22	1.00	Production sheet	Produced product, stored, and sent to xanthate process plant.

Background datasets

Background processes for both the old and new carbon disulphide production systems include the production of coal-based electricity and steam, fuel gas, nitrogen and molten sulphur. In terms of carbon sources, the background system for the old carbon disulphide production system included charcoal production, whilst that for the new carbon disulphide process system included production of natural gas in the form of methane. Other materials included in the background system for the new carbon disulphide production system are the additives used for purification of the molten sulphur, namely activated clay and lime. For both carbon disulphide production systems, treatment of solid waste, hazardous waste and wastewater was carried out in off-site facilities. The background systems also take into account the impacts associated with the transport of the carbon source to the production facility at Senmin®. Charcoal was transported by truck from Mpumalanga situated 500 km away, and natural gas is transported via pipeline form Mozambique, over a distance of 865km. Direct emissions from the foreground system (CS_2 process) were emitted to the environment. The CS_2 product was used for xanthate production.

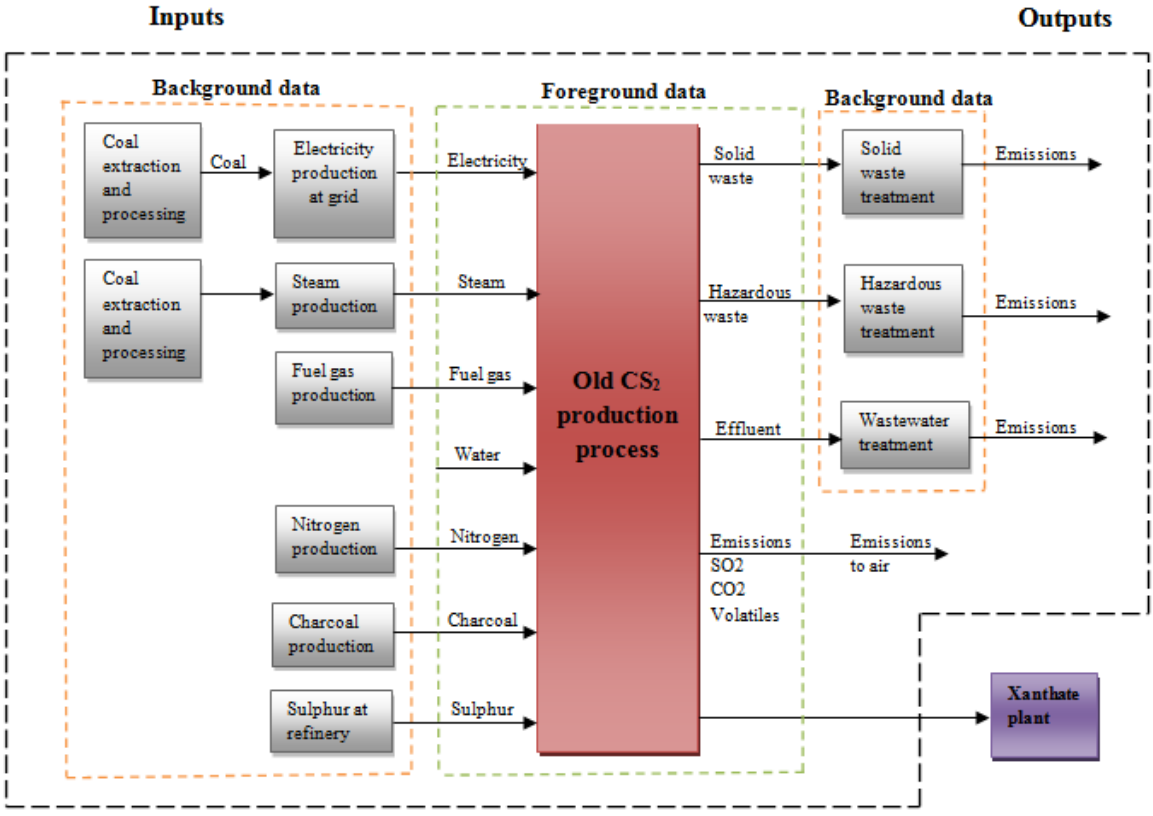


Figure 15: Old process system boundary for the production of carbon disulphide

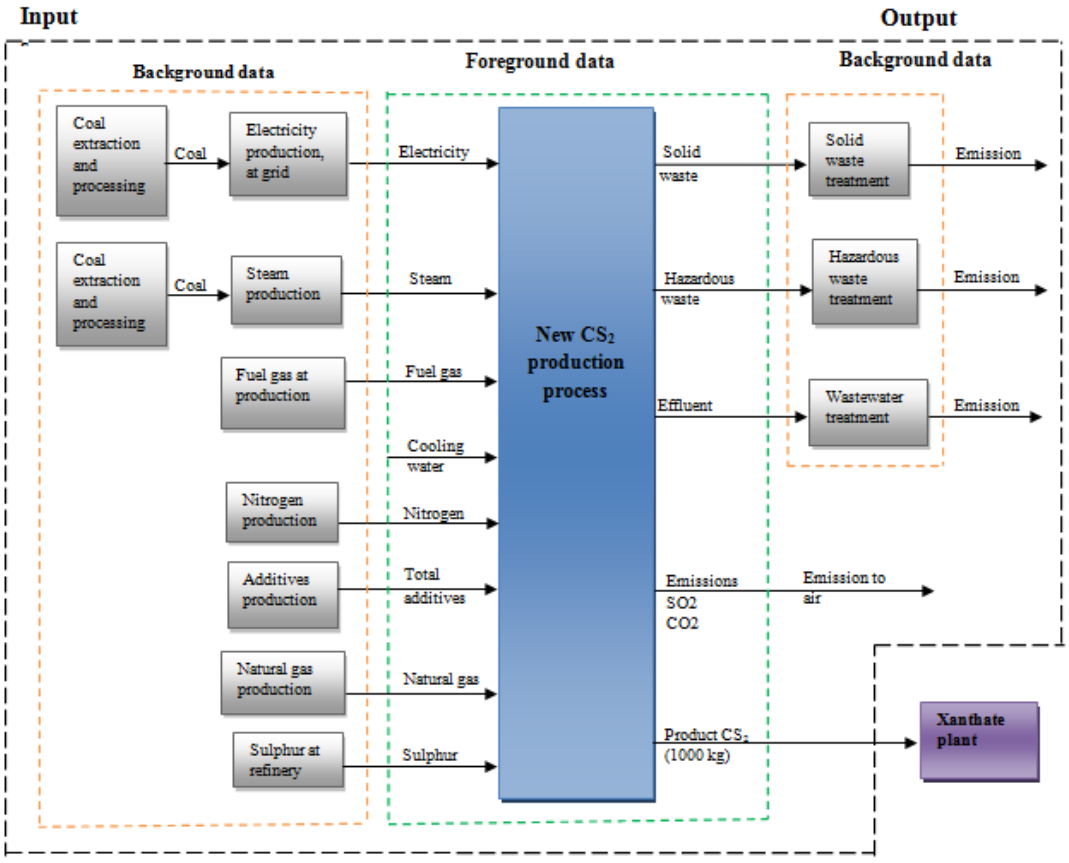


Figure 16: New process system boundary for the production of carbon disulphide

Data for the background systems was procured from ecoinvent version 2.2 (Hischier et al., 2009), except for the case of coal-based production of South African electricity production which was build using ecoinvent unit processes (Dick et al., 2012) . The catalyst used in the sulphur recovery process is excluded in the LCI due to the absence of information for this chemical in the databases. A summary of the background system databases used for this study is provided in Table 11. A more detailed description of the selected materials and processes in the databases is provided in Appendix E, where these datasets closely/better represent the used processes and materials in the study. Relevant emissions to the environment of the background systems for the old and new CS_2 process are provided in Table 12 and 13 respectively. These background emissions are essentially made up of both foreground elements (e.g. the quality of electricity consumed, solid waste produced etc.) and background elements (e.g. the emissions with electricity production and solid waste treatment).

Table 11: Summary of background process databases used in this study

Materials and Processes	Relevant System	Database	Time Period	Geography of Technology
Materials				
Sulphur	Old and New CS_2 process	Ecoinvent 2.2	2000	Europe
Charcoal	Old CS_2 process	Ecoinvent 2.2	2010	Europe
Natural gas	New CS_2 process	Ecoinvent 2.2	1991-2000	World
Nitrogen	Old and New CS_2 process, Xanthate process	Ecoinvent 2.2	2003	Europe, U.S.A, Russia
Lime	New CS_2 process	Ecoinvent 2.2	2003	Switzerland
Activation clay	New CS_2 process	Ecoinvent 2.2	2005	Switzerland
Carbon disulphide	Xanthate process	Created (this study)	2013	South Africa
Sodium hydroxide	Xanthate process	Ecoinvent 2.2	2003	Europe
Ethyl alcohol	Xanthate process	Ecoinvent 2.2	2007	Europe and India
Energy generation				
Electricity	Old and New CS_2 process, Xanthate process	Developed by UCT and The Green House	2012	South Africa
Fuel gas, natural gas	Old CS_2 process	Ecoinvent 2.2	2003	Switzerland
Steam, hard coal	Old and New CS_2 process, Xanthate process	Ecoinvent 2.2	1990	German
Natural gas	New CS_2 process	Ecoinvent 2.2	1991-2000	World
Waste treatment				
Solid waste	Old and New CS_2 process	Ecoinvent 2.2	2000	Switzerland
Hazardous waste	Old and New CS_2 process	Ecoinvent 2.2	2000	Switzerland
Effluent	Old and New CS_2 process	Ecoinvent 2.2	2000	Switzerland
Transportation				
Transport, lorry (>16t)	Old CS_2 process	Ecoinvent 2.2	2007	Switzerland
Transport, natural gas, pipeline	New CS_2 process	Ecoinvent 2.2	1994-2001	German

Table 12*: Background systems emissions arising from the production of 1 tonne CS_2 via the old process*

	Substance	Unit	Emissions per 1 tonne of CS_2										
			Charcoal (223.6 kg)	**Sulphur** (898.56 kg)	**Nitrogen** (49.57 m^3)	**Transport, lorry** (112.02 tkm)	**Electricity** (5.66 GJ)	**Steam** (12.73 GJ)	**Natural gas** (1.95 GJ)	**Solid waste treatment** (24.61 kg)	**Hazardous waste treatment** (8.45 kg)	**Wastewater treatment** (0.34 m^3)	**Total**
Outputs	CO_2, fossil	kg	23.4	276.93	24.07	14.20	1520.00	1550.00	5.54	12.29	20.15	0.11	3446.69
	SO_2	kg	0.16	28.55	0.08	0.02	12.39	8.52	0.08	0.00	0.01	0.00	49.81

Table 13: Background systems emissions arising from the production of 1 tonne CS_2 via the new process

	Substance	Units	Flows per 1 tonne of CS_2										
			Sulphur (881.78 kg)	**Total Natural gas** (593.34 m^3)	**Additives** (2.17 kg)	**Nitrogen** (13.05 m^3)	**Transport, pipeline** (318.21 tkm)	**Electricity** (0.81 GJ)	**Steam** (6.54 GJ)	**Hazardous waste treatment** (2.40 kg)	**Solid waste treatment** (1.86 kg)	**Wastewater treatment** (0.56 m^3)	**Total**
Outputs	CO_2, fossil	kg	271.75	62.91	0.14	6.25	16.61	213.00	797.13	5.72	0.04	0.18	1373.73
	SO_2	kg	28.02	0.93	0.00	0.02	0.01	1.78	4.38	0.00	0.00	0.00	35.14

4.2.2 Xanthate Production system

The system boundary for the liquid ethyl xanthate production process involves additional energy inputs in terms of electricity and steam, as well as raw materials (CS_2, sodium hydroxide and ethyl alcohol) used to produce xanthate. There are no direct emissions or wastes from this plant. The foreground and background system boundaries for the liquid ethyl xanthate production process are depicted in Figure 17.

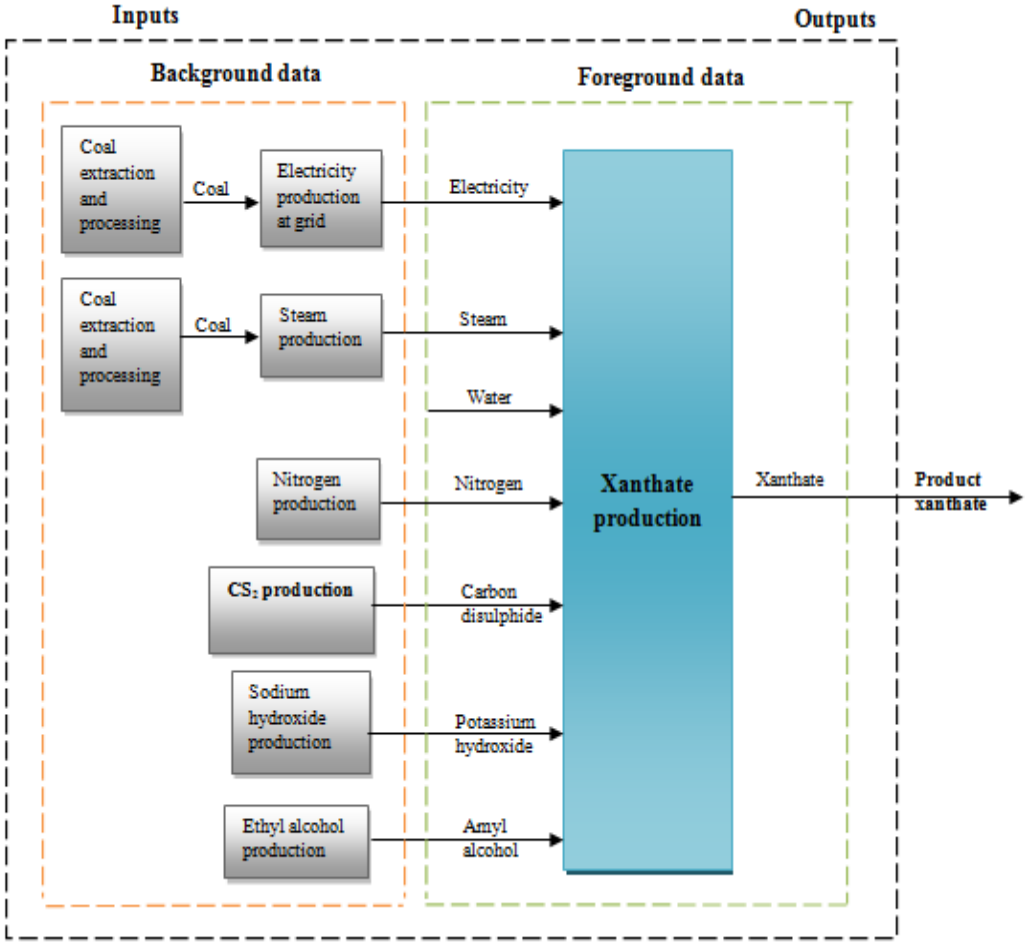


Figure 17: System boundary for the liquid ethyl xanthate production process.

Foreground parameters

Parameters were collected from the year 2011 annual production and a weighted average was calculated. The raw data is presented in Appendix D, Table D1. From the weighted average inputs and output were calculated based on 1 tonne CS_2 used (produced from old and new CS_2 process), as well as per pure unit xanthate produced. In cases where plant data was not available due to confidentiality or other reasons, data was derived from mass balance calculations. Detailed mass balances calculations are provided in Appendix D. Foreground process data for the liquid xanthate production process is summarised in Table 14.

Table 14: Foreground process data arising from the production of liquid xanthate (SEX) using 1 tonne CS_2

Description			Units	Per tonne of CS_2 used	Per unit xanthate produced	Data source	Comments
Inputs	Energy	Electricity	GJ	1.12	0.59	Production sheet	Electricity from the grid is used for plant equipment operations.
		Total energy	GJ	1.12	0.59	Production sheet	Total energy (Electricity only)
	Materials	Water	m^3	2.99	1.58	Production sheet	Water is used for dilution and cooling purposes
		Nitrogen	m^3	41.67	22	Production sheet	Nitrogen is used for purging of plant equipment
		CS_2	tonnes	1.00	0.53	Calculated	Assuming 100% stoichiometric amount.
		Alcohol	tonnes	0.61	0.32	Calculated	Alcohol fresh feed, assuming 100% stoichiometric amount and 10% is recycled.
		Caustic	tonnes	0.53	0.28	Calculated	Assuming 100% stoichiometric amount
Output	Product	Xanthate (100%)	tonnes	1.89	1.00	Calculated	Based on 40% purity of SEX (CH3CH2OCS2Na)

Background datasets

Background processes for liquid ethyl xanthate include the production of coal-based electricity and steam, nitrogen, carbon disulphide, sodium hydroxide and ethyl alcohol. Background data was procured from ecoinvent version 2.2 (Hischier et al., 2009), except for the case of coal-based production of South African electricity production which was build using ecoinvent unit processes (Dick et al., 2012), and carbon disulphide production process (created in this study). A summary of the background system databases used for this study is provided in Table 11 (page 62). A more detailed description of the databases is provided in Appendix E.

4.3 Life cycle impact assessment (LCIA)

This section presents and discusses the results of the life cycle impact assessment modelling for the carbon disulphide (subsection 4.3.1) and xanthate (subsection 4.3.2) production systems.

4.3.1 Carbon disulphide production

The inventory data derived in section 4.2 was used as input data for modelling the life cycle impacts of the old and new carbon disulphide process systems, using the Simapro software (version 7.3.3) and ReCiPe midpoint method. Five impact categories were selected for this assessment, namely climate change, terrestrial acidification, human toxicity, freshwater ecotoxicity and fossil depletion. From an environmental perspective, the results in Figure 18 show that the new CS_2 process performs better than the old process in all the impact categories investigated, particularly in the case of climate change (54%), human toxicity (49%) and freshwater ecotoxicity (58%). There are slight improvements in terrestrial acidification (14%) and fossil depletion (11%).

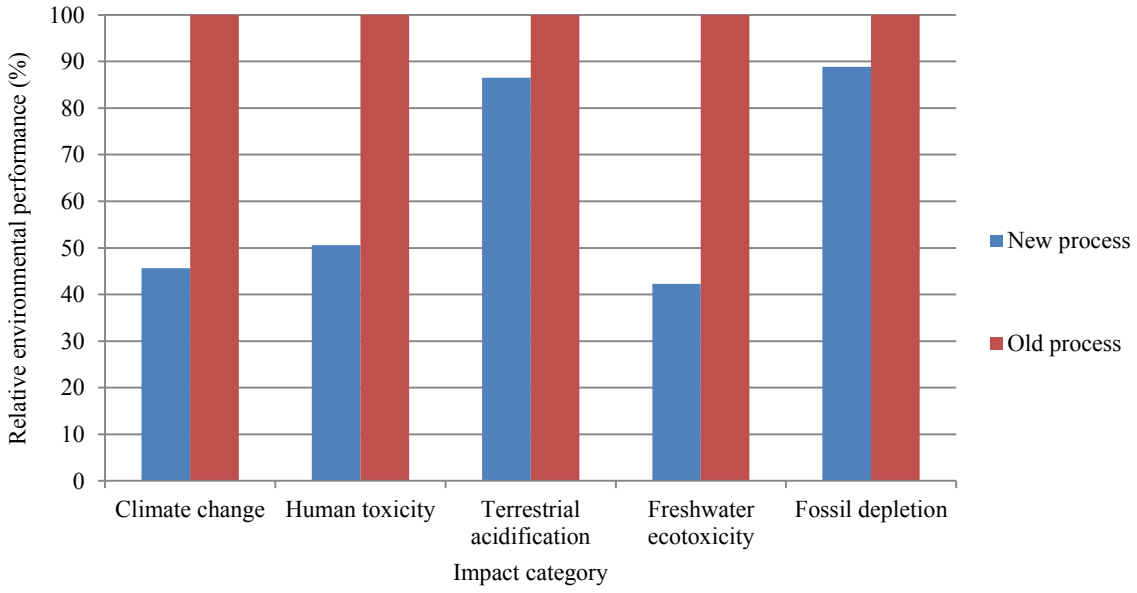


Figure 18: Relative environmental performance for the production of 1 tonne CS_2 via the new and old processes

Process contribution to impact categories

Figures 19 and 20 show the relative process contribution to each of these impact categories for the old and new CS_2 production systems respectively. These contributions are discussed in the subsections below. Detailed results are presented in Appendix F, Table F1.

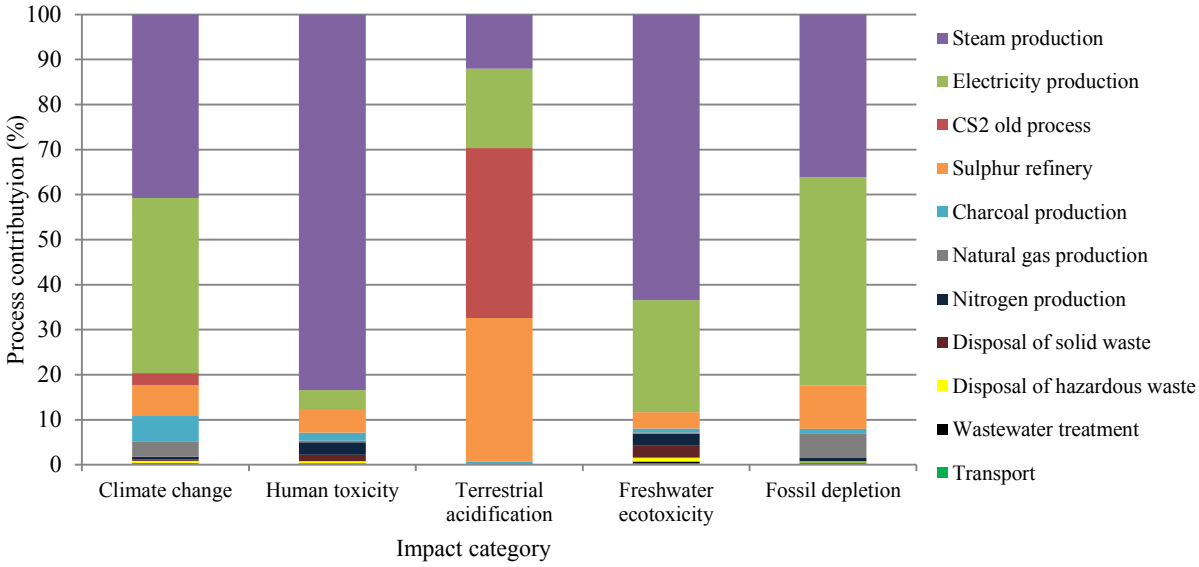


Figure 19: Material and process contributions (% of total) to the potential environmental impacts arising from the production of 1 tonne CS_2 via the old process

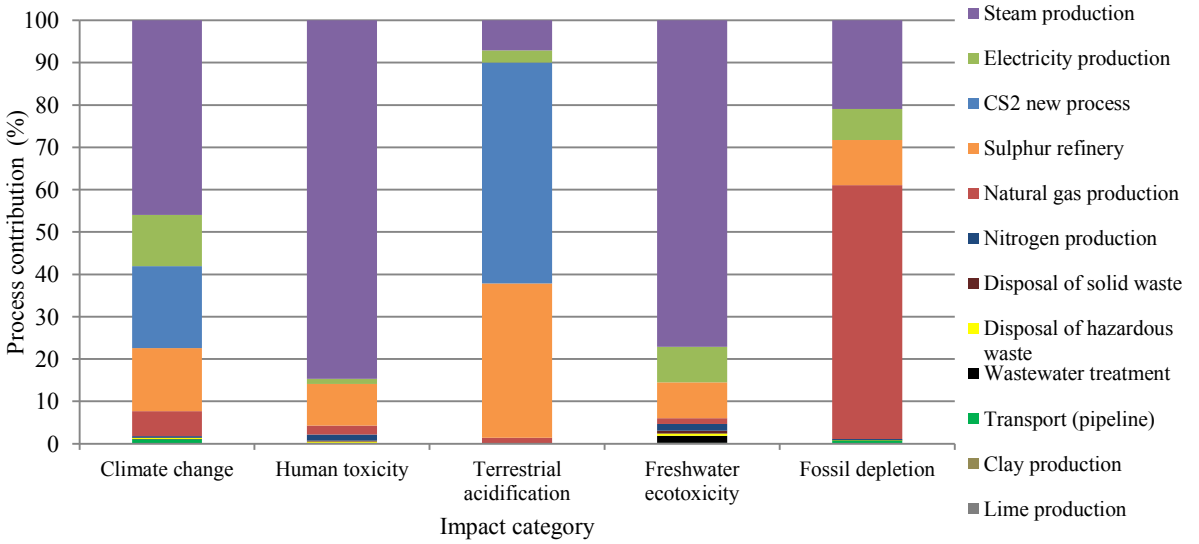


Figure 20: Material and process contributions (% of total) to the potential environmental impacts arising from the production of 1 tonne CS_2 via the new process

- **Climate change**

Figures 19 and 20 indicate that climate change impacts for both processes are dominated by the background production of steam and electricity. Processes contributing to the emissions of greenhouse gases are compared in detail for the two processes in Figure 21.

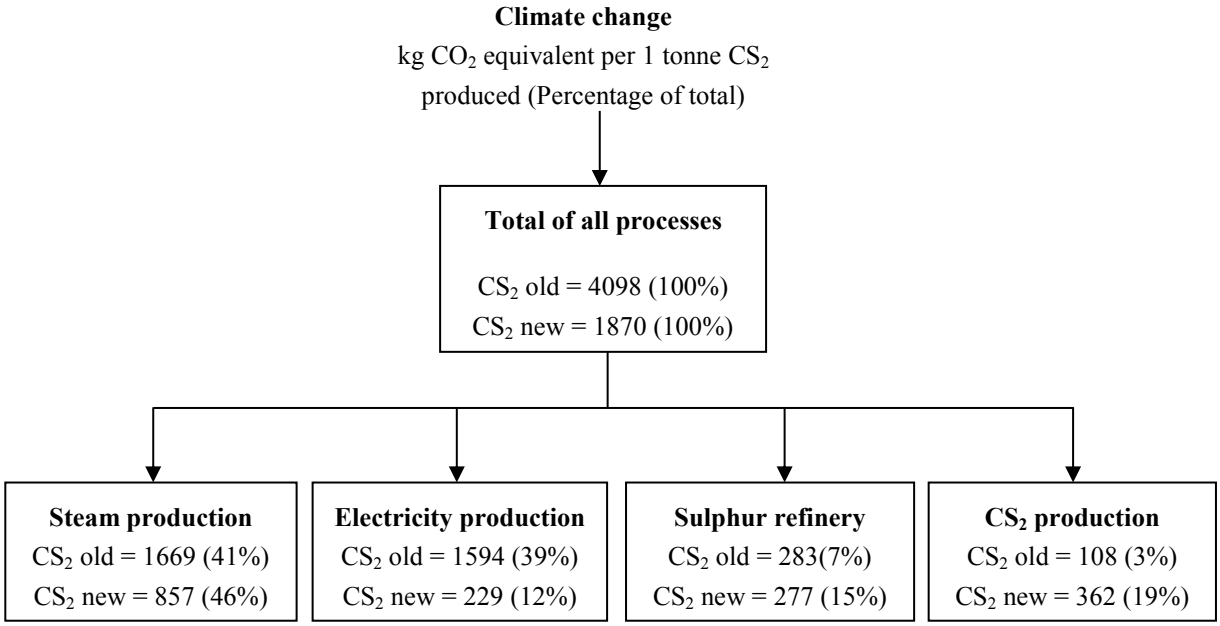


Figure 21: Material and process contributions to climate change impact category arising from the production of 1 tonne CS_2 for the two processes

The old CS_2 process makes a significantly higher contribution to climate change than the new process (4098 vs 1870 kg CO_2 equivalents). The major contribution in both cases is from the production of steam (42% of total) and, in the case of the old carbon disulphide process, steam and electricity (41% and 39% of total respectively). Both steam and electricity are produced from the mining of coal, and its combustion is a major contributor to greenhouse gases that cause climate change. The sulphur refinery also makes a substantial contribution to climate change for both the old and new CS_2 processes (283 and 277 kg CO_2 equivalents respectively). However, the new CS_2 production process itself contributes a larger portion of CO_2 (362 kg CO_2 equivalents) as compared to the old process (108 kg CO_2 equivalents) and this can be attributed to the higher use of natural gas for energy (70% more) than the old CS_2 process, as indicated in the foreground data analysis (subsection 4.2.1, Table 8).

- **Human toxicity**

Figure 22 provides a comparison of the processes contributing to human toxicity during carbon disulphide production.

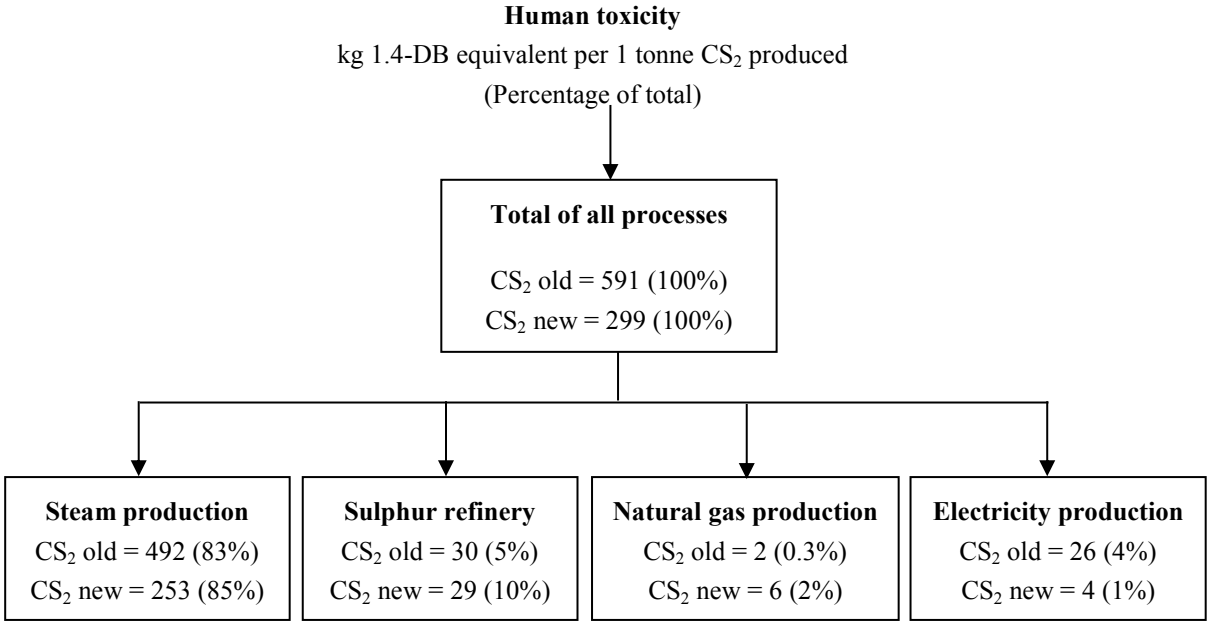


Figure 22: Material and process contributions to human toxicity impact category arising from the production of 1 tonne CS_2 for the two processes

The human toxicity impacts of the old carbon disulphide process are double that of the new carbon disulphide process. Figure 22 shows a total contribution of 591 kg 1.4 DB equivalents per CS_2 produced for the old process and the new process having a lower contribution of 299 kg 1.4 DB equivalents. The dominating process in the case of both CS_2 production routes is the production of steam, which is associated with coal mining and combustion, contributing 85% for the new process (253 kg 1.4 DB equivalent out of a total of 299 kg 1.4 DB equivalent per tonne of CS_2 produced) and 83% for the old process (492 kg 1.4 DB equivalent out of a total of 591 kg 1.4 DB equivalent per tonne of CS_2 produced). This can be attributed to the high usage of steam for the old CS_2 process as seen in the foreground data analysis (subsection 4.2.1, Table 8)

Sub-processes that contribute to this impact category are: sulphur, at refinery, with the new CS_2 process contributing 10% (29 kg 1.4 DB equivalent per CS_2 produced) and the old process contributing a total of 5% (30 kg 1.4 DB equivalent per CS_2 produced); natural gas production makes a relatively small contribution 0.3% (2 kg 1.4 DB equivalent) for the old process and 2% (6 kg 1.4 DB equivalents) for the new process; electricity production with a

contribution of 4% (26 kg 1.4 DB equivalents) for the old process and 1% (4 kg 1.4 DB equivalent) for the new process.

- **Terrestrial acidification**

Terrestrial acidification results when atmospheric deposition of inorganic substances, such as sulphates, nitrates, and ammonia, become trapped in rain and cause impacts on soil and water bodies. This impact category is expressed relative to the acidifying effect of sulphur dioxide (SO_2). Processes contributing to this impact category for the compared CS_2 processes are shown in Figure 23.

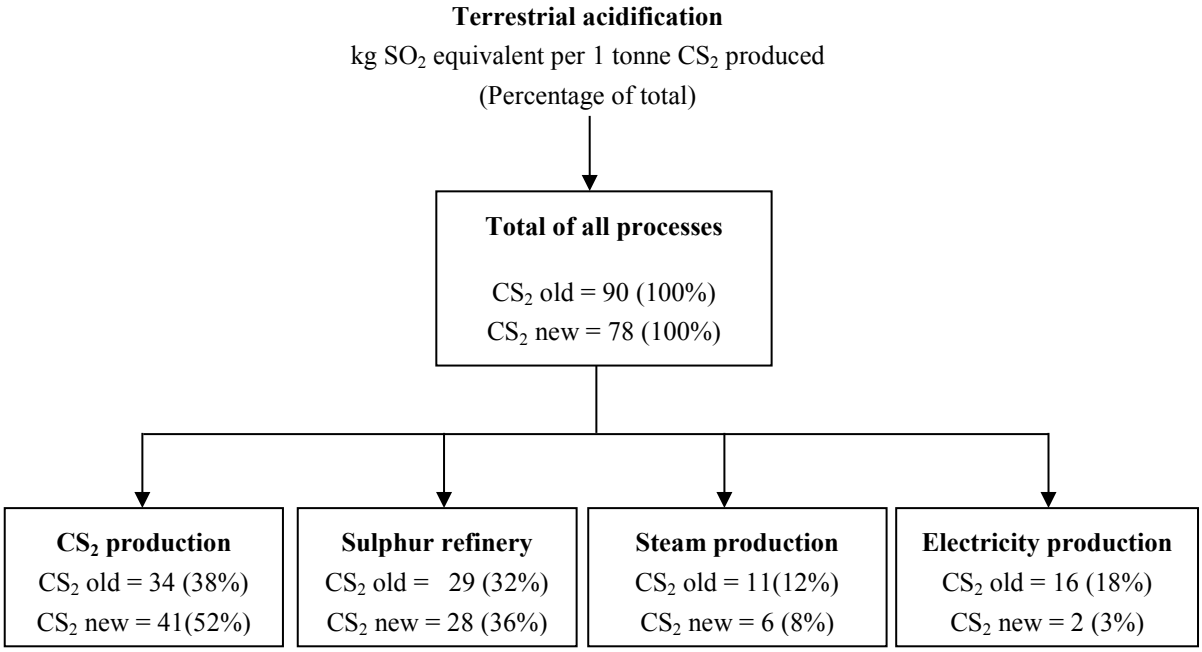


Figure 23: Material and process contributions to terrestrial acidification impact category arising from the production of 1 tonne CS_2 for the two processes

The production of carbon disulphide for both the new and old process is a major contributor in this impact category, with the new process having a higher contribution of 52% (41 kg SO_2 equivalents per CS_2 produced) than the old process, which contributes 38% (34 kg SO_2 equivalents per CS_2 produced). Major sub-processes in this category are; sulphur refinery, steam production and electricity production, where the old CS_2 process makes a substantial contribution of 32% (29 kg SO_2 equivalents per CS_2 produced), 12% (11 kg SO_2 equivalents per CS_2 produced) and 18% (16 kg SO_2 equivalents per CS_2 produced) respectfully.

- **Freshwater ecotoxicity**

Figure 18 show that the new CS_2 process makes significantly less contribution (42%) towards fresh water ecotoxicity than the old process. Figure 24 shows the processes contributing to fresh water ecotoxicity impact category for the new and old CS_2 processes.

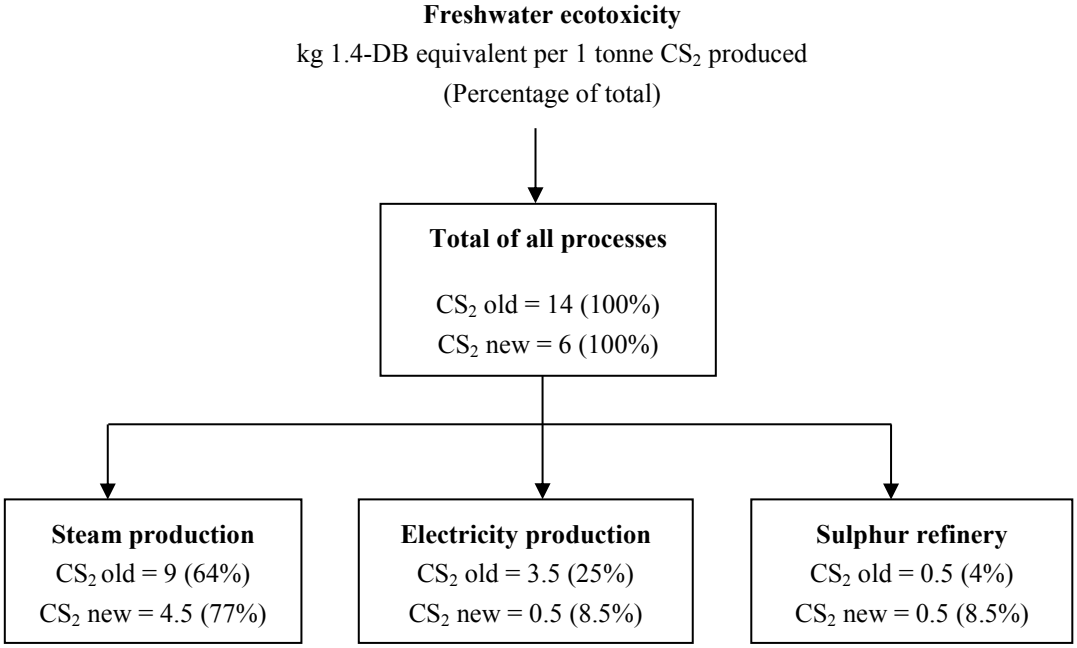


Figure 24: Material and process contributions to freshwater ecotoxicity impact category arising from the production of 1 tonne CS_2 for the two processes

As in the case of the impacts contributing to human toxicity, steam production, which is associated with coal mining, is the dominating process in this category, making a contribution of 64% (9 kg 1.4 DB equivalents per CS_2 produced) for the old CS_2 process and 77 % (5 kg 1.4 DB equivalents per CS_2 produced) for the new CS_2 process. Sub-processes contributing to this impact category have lower percentage contributions. Electricity production for the old CS_2 process has a substantial contribution of 25% (3.5 kg 1.4 DB equivalents per CS_2 produced) as compared to 8.5% (0.5 kg 1.4 DB equivalents per CS_2 produced) for the new CS_2 process. This is due to the large amount of electricity that was used in this process as previously seen in the foreground data analysis (Table 8). Sulphur refinery, makes a lower contribution of 4% for the old CS_2 production process and 8.5% for the new process.

- **Fossil depletion**

Processes contributing to fossil depletion are compared for the old and new CS_2 production processes in Figure 25.

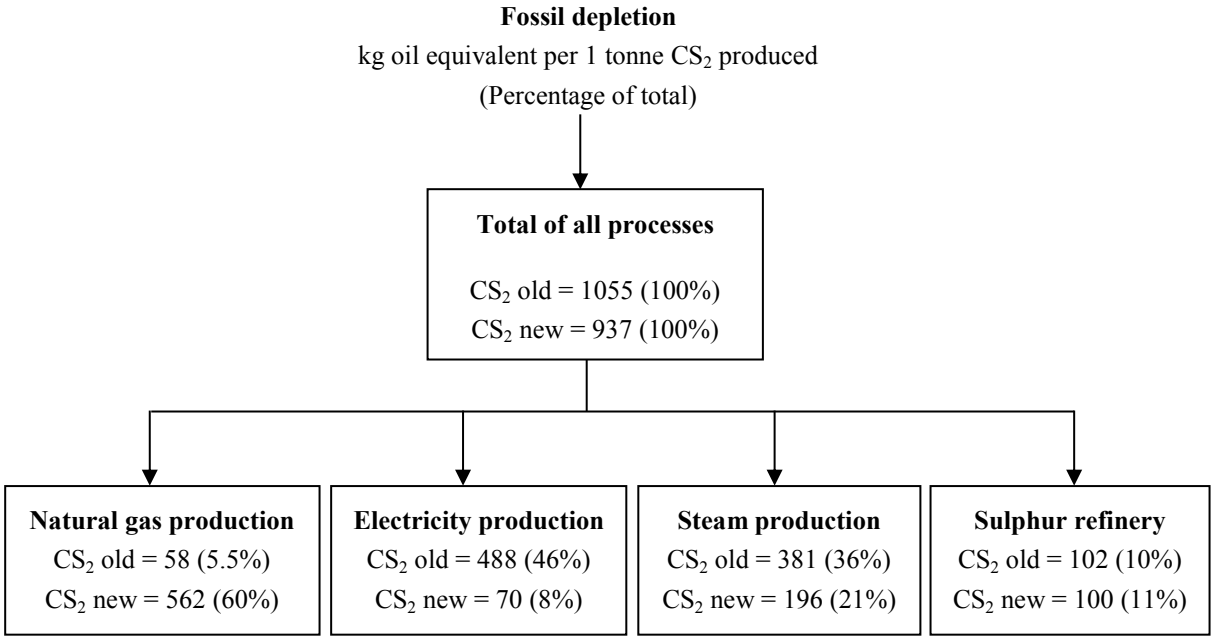


Figure 25: Material and process contributions to fossil depletion impact category arising from the production of 1 tonne CS_2 for the two processes

Natural gas production is a major contributor to fossil depletion in the new CS_2 process by 60% (562 kg oil equivalents per CS_2 produced) as compared to the old process (5.5%). This is due to the use of this gas as a raw material and energy source in the production process. Major sub-processes also contributing to this impact category are electricity production, which has a significant contribution for the old CS_2 process (488 kg oil equivalents per CS_2 produced), as compared to the new process (70 kg oil equivalents per CS_2 produced). The production of steam contributes 36% (381 kg oil equivalents per CS_2 produced) in the case of the old CS_2 process and 21% (196 kg oil equivalents per CS_2 produced) in the case of the new process. The sulphur recovery process makes a relatively low contribution for both CS_2 processes (less than 11%).

Effect of net steam consumption

As previously shown in Figures 19 and 20, the consumption of steam contributes significantly to the environmental footprint of CS_2 production for both process routes. A comparison of plant design and current performance indicates that there are opportunities to improve steam recovery. On this basis an analysis is done to explore further the potential

effects of improving steam recovery in the new process since this process generates its own steam. Figure 26 shows that improving the recovery and reuse of generated steam such that there is zero net steam consumption will result in further improvements in the environmental performance of the new process across all categories, making a significant reduction to climate change from 54% to 75%, human toxicity from 49% to 93%, freshwater ecotoxicity from 58% to 90%. A slight improvement is made to terrestrial acidification (from 13% to 19%) and fossil depletion (from 11% to 30%).

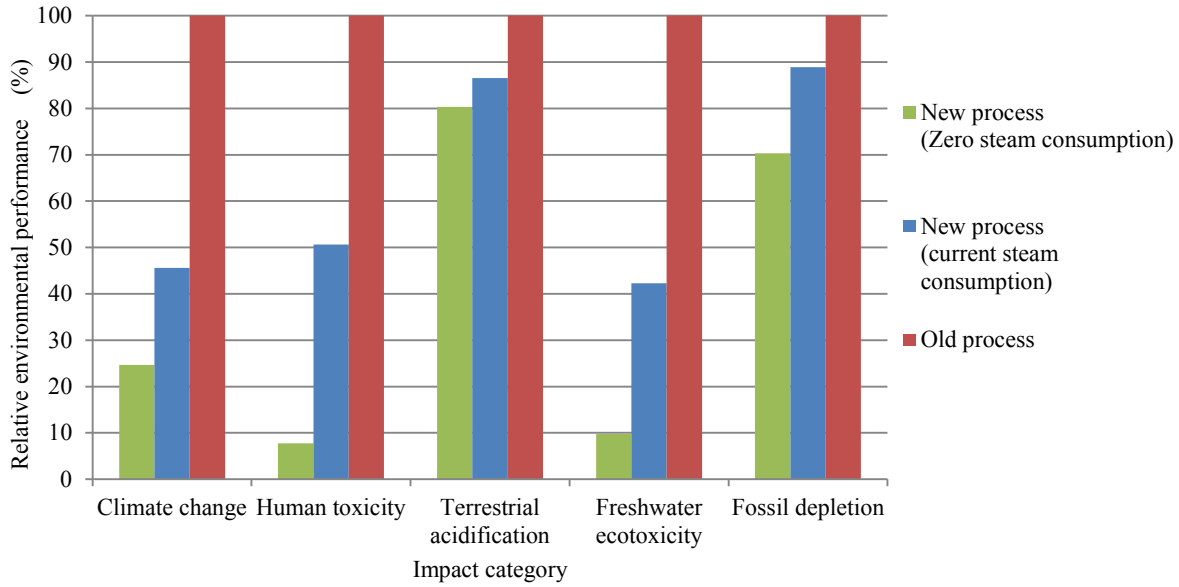


Figure 26: Analysis results testing the relative environmental performance arising from the production of 1 tonne CS_2 for the new process

4.3.2 Xanthate impact assessment

Using 1 tonne of CS_2 process (functional unit) to produce liquid xanthate, the LCA results in Figure 27 show that xanthate produced via the new CS_2 process has a reduced environmental impact compared to that produced by the old CS_2 processes across all impact categories; climate change (39% reduction), human toxicity (23% reduction), terrestrial acidification (12% reduction), freshwater ecotoxicity (32% reduction) and fossil depletion (6% reduction).

As shown previously in Figure 18, the new process has positive effects on the xanthate production process with a noticeable reduction in climate change impacts (Figure 27). Climate change is now down by 54% for CS_2 production (Figure 18), which means that for the xanthate process it is now 39% less CO_2 intensive. The reduction also applies to the other impact categories as indicated above. Since the results of the new carbon disulphide have a positive effect on xanthate production, these are analysed as part of the processes contributing to the impact categories of xanthate.

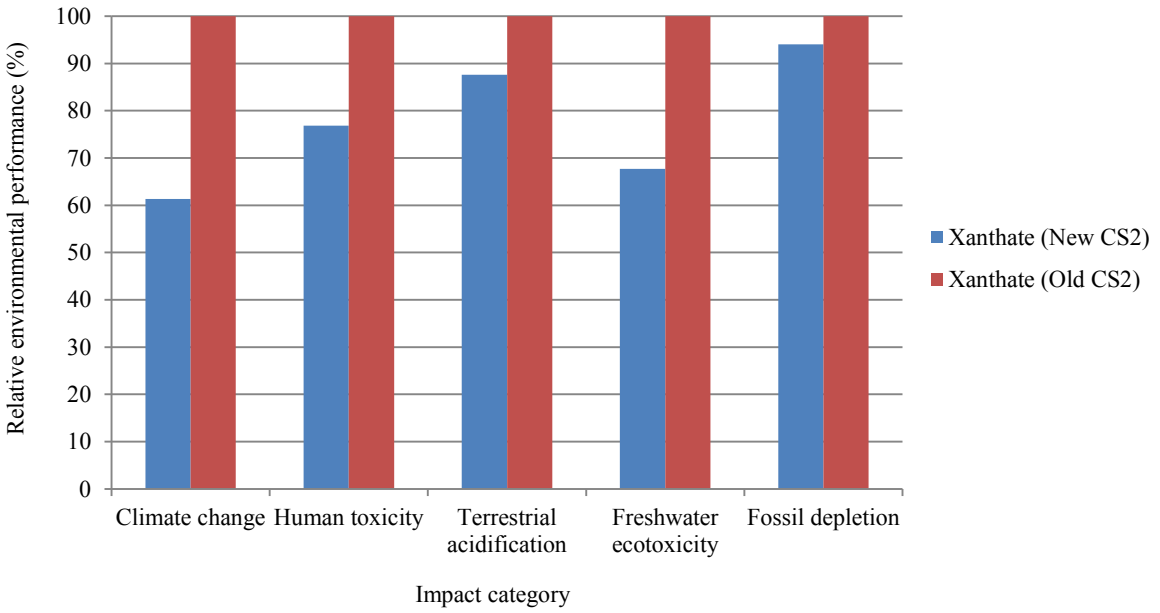


Figure 27: Relative environmental performance arising from the use of 1 tonne CS_2 via the new and old process for xanthate production

Process contributions to impact categories

Processes contributing to the environmental performance of xanthate product (Figure 28) are mostly impacts associated with background processes, particularly the production of carbon disulphide, sodium hydroxide and alcohol.

Carbon disulphide impacts largely dominate xanthate's total terrestrial acidification (91%). This is due to the emissions of SO_2 in the new CS_2 production process that make a significant contribution of 52% to terrestrial acidification as seen in Figure 20 and 23 previously. This process also makes a substantial contribution to xanthate's climate change (53%), fossil depletion (50%), fresh water ecotoxicity (34%) and human toxicity (30%).

The production of caustic contributes a large portion of total human toxicity (60%) and fresh water ecotoxicity (51%). To a lesser extent, caustic production contributes to the impact categories of climate change (16%) and fossil depletion (9%), and relatively less to terrestrial acidification (3%).

Alcohol production contributes substantially to the impact categories of fossil depletion (36%) and climate change (21%). To a lesser extent, the production of alcohol contributes to human toxicity, terrestrial acidification and freshwater ecotoxicity (8%, 2% and 8% respectively).

The production of xanthate does not use much electricity. This is consistent with the significantly low contribution of electricity production to all the impact categories (Figure 28 and Appendix A3). Electricity production only contributes between 4% and 9% across the impact category.

Less important to xanthate's life cycle is the production of nitrogen. Production of nitrogen makes a relatively low contribution in terms of climate change, human toxicity and fresh water ecotoxicity (1%, 1% and 2% respectively). The production of nitrogen impacts to terrestrial acidification and fossil depletion are insignificant.

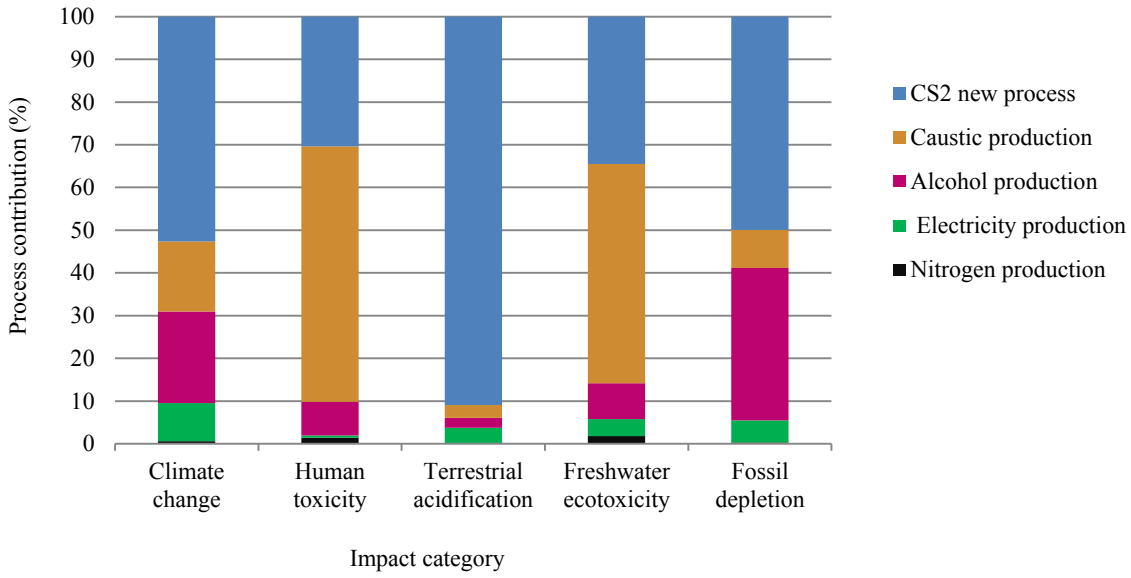


Figure 28: Material and process contributions (% of total) to the potential environmental impacts arising from the use of 1 tonne CS_2 from the new process to the xanthate process

Chapter 5

LIFE CYCLE ASSESSMENT OF XANTHATE UTILISATION IN ARD MITIGATION

The goal of the second life cycle assessment study is to assess and compare the environmental benefits and/or impacts of a desulphurisation flotation and conventional treatment and management processes for the base metal sulphide tailings, insofar as xanthate is used as a sulphide collector in the desulphurisation process. This chapter of the dissertation presents and discusses the results of this life cycle assessment study, and includes a description of the tailings treatment and management processes, the life cycle inventory, impact assessment modelling, interpretation of model outcomes.

5.1 Description of the tailings management scenarios

As discussed in Chapter 2 (subsection 2.3.1), the mining industry generates large volumes of solid waste, i.e. waste rock and tailings, which can have significant environmental impacts, one of the most serious of which is acid rock drainage (ARD). In the next subsections, two tailings management processes were compared (as per methodology described in Chapter 3); the conventional and desulphurisation flotation treatment process (subsections 5.1.1 and 5.1.2 respectively).

5.1.1 Conventional tailings treatment (base case)

The flow diagram for the conventional treatment of large-volume mine tailings is shown in Figure 39.

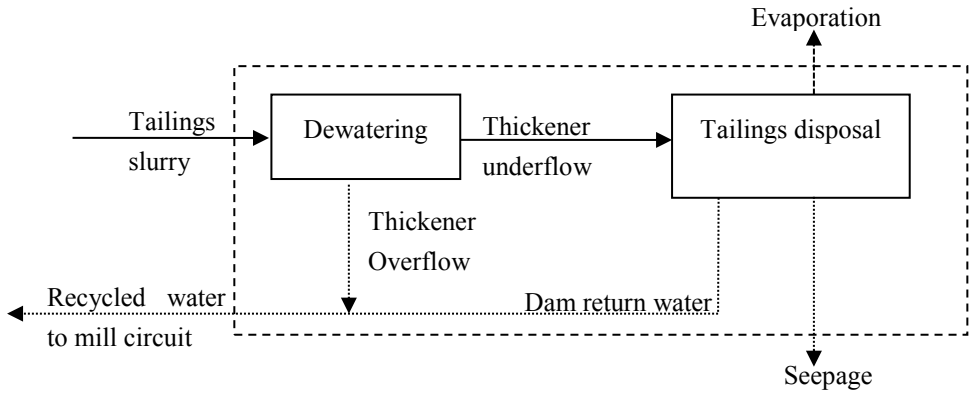


Figure 29: Process flow diagram for the conventional tailings treatment and management scenario

The tailings are usually dewatered in conventional thickeners (cylindrical and continuous) to about 55 – 65% by weight (Mwale, 2005: Donoso et al., 2013), with the thickener overflow generally being recycled back to the mill circuit. Tailings slurry underflow is discharged by using either cycloning or spigoting to specially designed impoundments formed by a contaminated dyke, constructed of suitable fill material. The tailings are allowed to settle from suspension to a deposit that is stable. The deposits release significant amounts of water which is typically controlled through decantation by means of an embankment drain, decant towers or a floating pump. Recovered tailings dam water is recycled and used in the mill circuit. Dissipative water loss occurs through evaporation (typically 5–40% of tailing water), seepage (typically 5% of tailing water) and entrainment (30–50% of tailing water) (Bleiwas, 2012).

Continued generation of contaminated leachate (acid drainage) from sulphide bearing waste contains soluble acid, salts and metals formed through the reaction of residual sulphides and acid neutralising carbonate minerals in the tailings during disposal, as well as residual flotation chemicals. Acid drainage generation occurs as a result of water and oxygen coming into contact with solid waste as explained in the literature review (Chapter 2, section 2.3). The contaminated leachate seeps through the tailings impoundment and eventually gets into contact with ground water. This can result in adverse consequences in terms of biodiversity conservation, quality of water and soil as well as health impacts (Broadhurst et al., 2007b; Harrison et al., 2010). Therefore, the deposit is considered as a unit operation generating its own emissions to air (water vapour), water (seepage) and land (unreacted tailings), as well as a product output in the form of recovered water.

5.1.2 Desulphurisation flotation management scenario

The desulphurisation flotation management option consists of the following operating stages: (1) flotation that produces two fractions, the sulphide rich concentrate and the sulphide-lean tailings; (2) dewatering of the two fractions; and (3) final disposal of the tailings in the tailings storage facility. Figure 30 depicts the flow diagram of the management scenario incorporating the desulphurisation flotation treatment process.

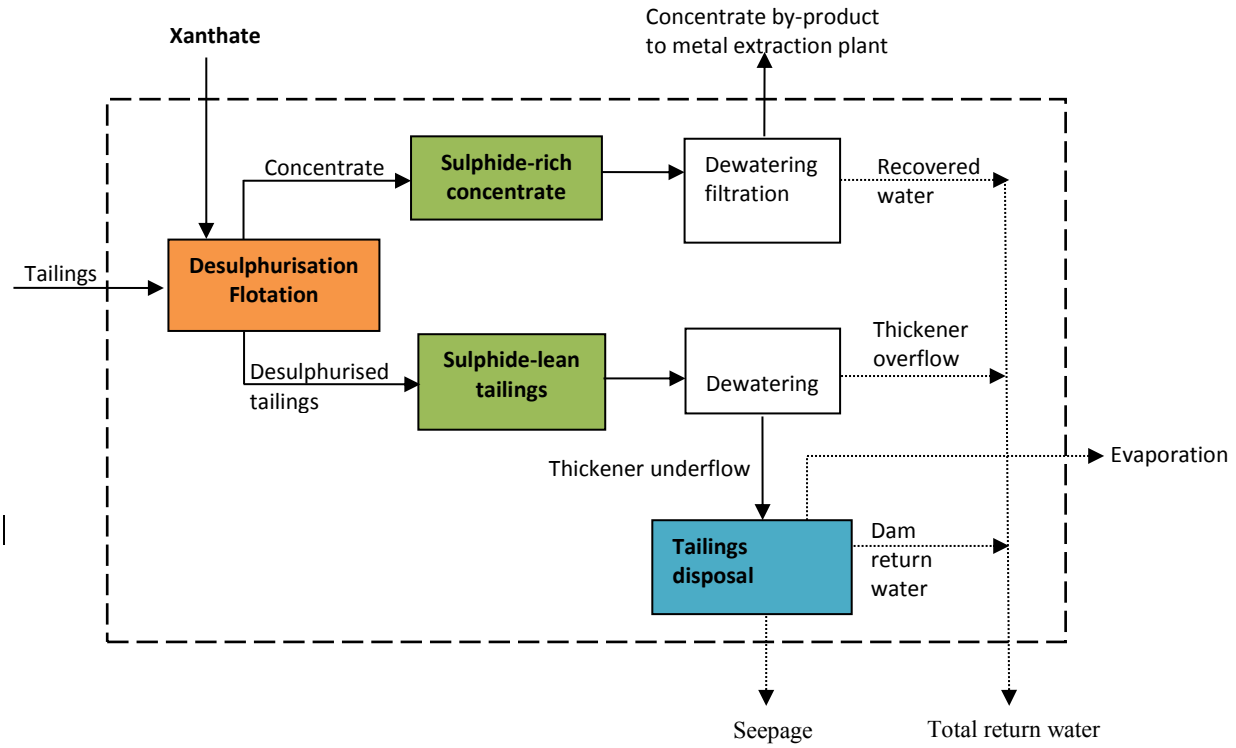


Figure 30: Process flow diagram for the desulphurisation tailings management scenario

Conventional tailings from a beneficiation separation unit are sent to the desulphurisation flotation circuit where a sufficient quantity of sulphides are separated into two fractions: a large volume of sulphide-lean tailings stream, which is non-acid forming, and a smaller volume of sulphide-rich concentrate, that is acid generating. The conventional feed tailings are expected to have minor xanthate from conventional flotation process. Xanthate collector, which is characterised by its ability to collect for sulphide minerals, is used for the non-selective flotation of the sulphide mineral in this process. Other reagents such as the frother and modifier are added to promote sulphur recovery and concentrate grade. These reagents, as well as the xanthate, are mixed with the tailings at a consistent airflow introduced into the unit. The flotation slurry typically contains 30% solids.

After separation, the sulphide-rich concentrate is dewatered by means of filtration (moisture content of around 10% by weight) to produce a sulphide-rich by-product which can be recycled to the primary metal extraction circuit for further processing to produce acid and or base metal values. Most of the xanthate is retained on the sulphide minerals collected as concentrate and gets destroyed when dried in the smelter after flotation (NICNAS, 1995). Similar to the conventional tailings disposal, explained in the previous section, the sulphide-lean tailings produced from the desulphurisation flotation process is subsequently subjected to dewatering and disposal.

5.2 Life cycle inventory (LCI) analysis

The inventory analysis of this study identifies and quantifies energy and material usage as well as environmental releases. This section describes the system boundaries and relevant parameters for the treatment and management of sulphidic tailings for the conventional scenario (subsection 5.1.1) and the desulphurisation flotation scenario (subsection 5.1.2).

The overall system boundaries, depicting both the background (off-site processes which supply inputs to the foreground system) and foreground (primary data) sub-systems for the conventional and desulphurisation processes are presented in Figures 31 and 32 respectively. Life cycle inventory modelling for each of these systems was conducted using the Simapro Software (version 7.3.3) package, at a reference flowrate of 100 tonnes of dry tailings per day.

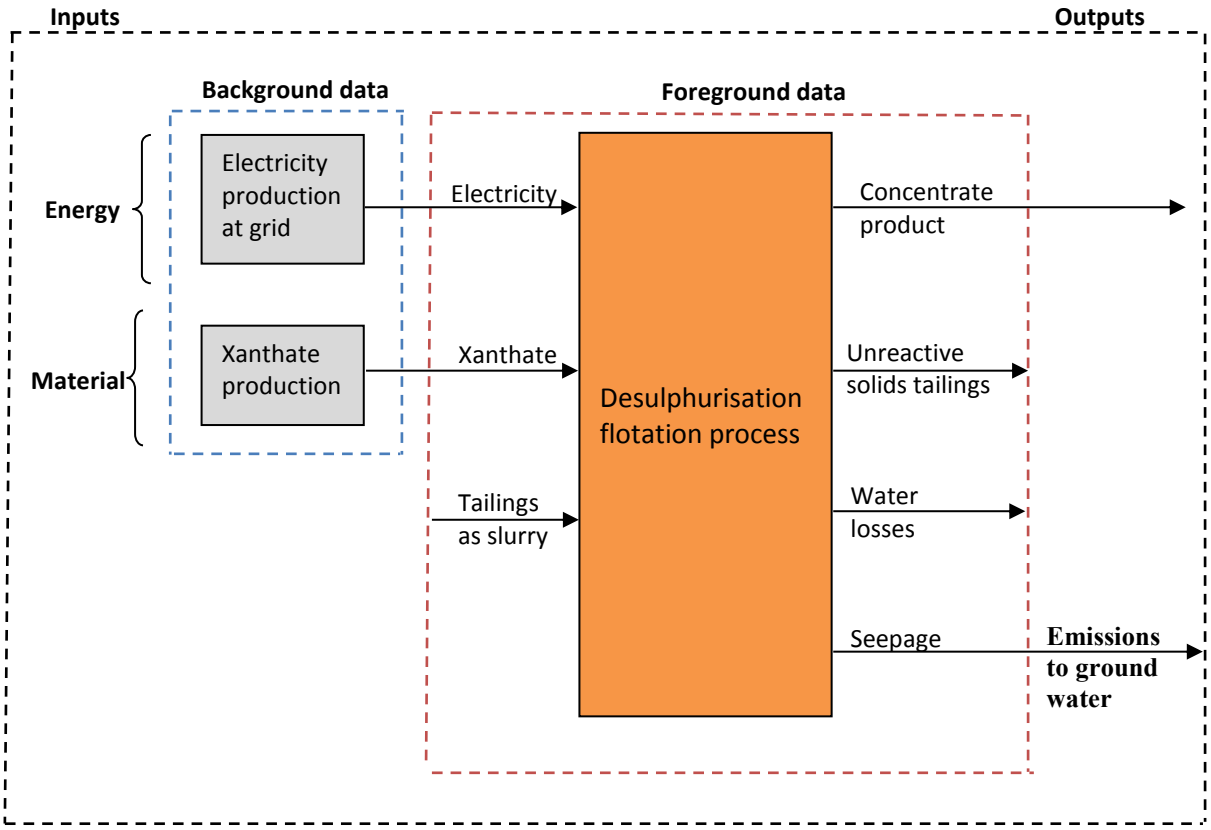


Figure 31: Overall system boundary for the desulphurisation flotation tailings management scenario

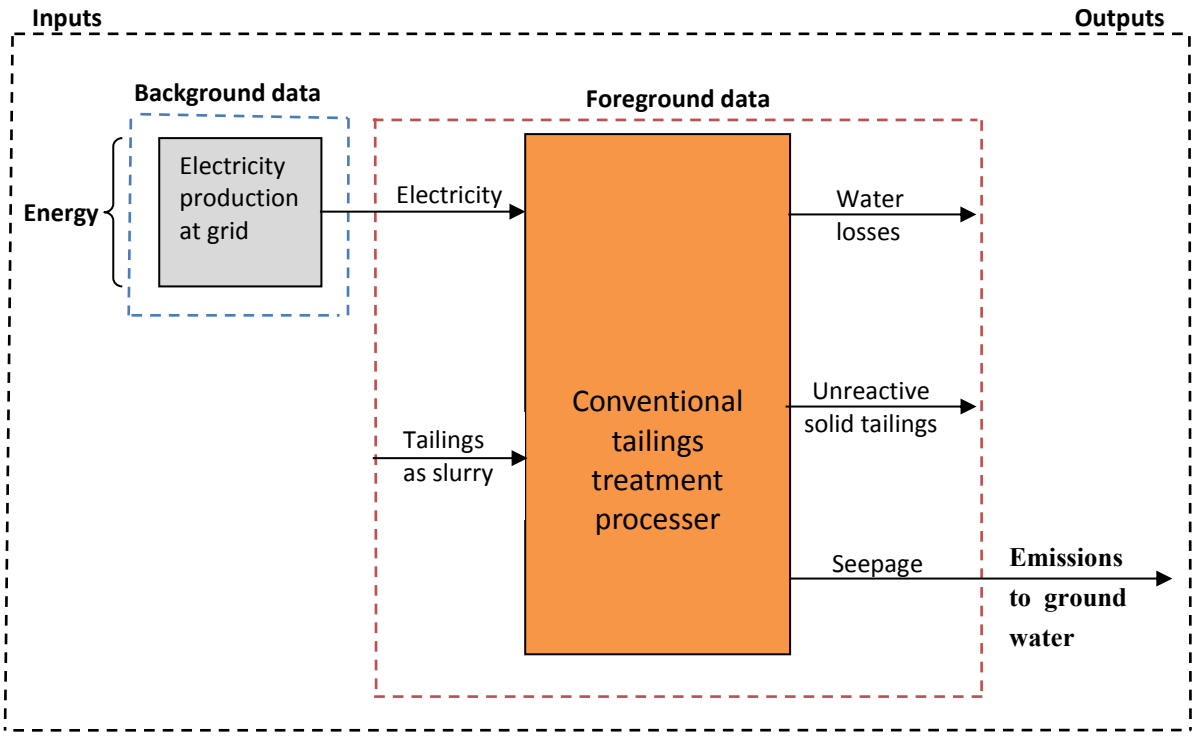


Figure 32: Overall system boundaries for the conventional tailings management scenario (base case)

5.2.1 Foreground datasets

Input and output data for the foreground sub-systems for both tailings management scenarios was derived from a combination of literature information, in-house knowledge and mass balance calculations.

The composition of the feed tailings, dosage of xanthate and deportment of desulphurised tailings were obtained from a base metal case study by Benzaazoua and Kongolo (2003). Relevant data from this case study is summarised in Table 15

Table 15: Deportment of sulphide minerals – Base metal case study

	Feed tailings (%)	Desulphurised tailings (%)	Sulphide-rich concentrate (%)	Percentage removal (%)
Minerals				
Pyrite	17.40	2.18	56.53	91[1]
Sphalerite	0.19	0.02	0.62	90
Chalcopyrite	0.10	0.07	0.19	61
Calcite	2.70	3.38	0.96	10[2]
Other (gangue)	79.61	94.36	41.67	15[1]
Sulphide sulphur	9.38	1.17	30.49	91
Total solids	100	100	100	28

[1]Derived from mass balance calculations; [2]assumed on the basis of literature information (Broadhurst et al., 2007b).

The main sulphide mineral studied in the case study was pyrite with 9.38% sulphur content. Using xanthate at a concentration of 90g/tonne of ore, 91% sulphur recovery was achieved (Table 15). Detailed mass balances calculations and assumptions for the desulphurisation treatment scenario are provided in Appendix G, Table G2. Foreground process data is summarised in Table 16 (page 82). For the base case scenario, detailed mass balances calculations and assumptions are provided in Appendix H, Table H2. Foreground process data is summarised in Table 17 (page 83).

Table 16: Foreground process data arising from the management of 100 tonnes of solid tailings – Desulphurisation flotation

Description			Units	Flows per 100 tonnes of solid tailings per day	Data source	Comments[1]
Inputs	Energy	Electricity	kJ	1 630 000	Marsden *et al*., (2008)	Electricity from the grid used for flotation tailings treatment
	Material	Tailings slurry (based on a solids content of 30% solids)	tonnes	333.33	Calculated	Feed tailings slurry. Calculation based on the addition of solids and water. Xanthate in slurry is assumed to be 1.5ppm NICNAS (2000)
		Xanthate	kg	9.00	Benzaazoua and kongolo, (2003)	Xanthate feed used for desulphurisation flotation.
Outputs	Waste streams	Tailings to disposal	tonnes	72.00	calculated	Assume 30 % entrainment of tailings water
		Water evaporation	tonnes	19.20	calculated	Assume 40% evaporation of tailings water
		seepage	tonnes	2.40	calculated	Assume 5% seepage of tailings water
	Emissions to ground water	Acid (H+)	kg	0.59	Calculated	Total acid (H+) in seepage. Calculations based on Net neutralisation potential (NNP) calculations.
		Sulphate (S)	kg	96.48	Calculated	Total sulphate in seepage. Assuming 80% net mobilisation of S in tailings pore water.
		Calcium (Ca)	kg	83.48	Calculated	Total calcium in seepage. Assuming 60% net mobilisation of Ca in tailings pore water.
		Copper (Cu)	kg	0.08	Calculated	Total copper in seepage. Assuming 5% net mobilisation of Cu in tailings pore water.
		Zinc (Zn)	kg	1.11	Calculated	Total zinc in seepage. Assuming 60% net mobilisation of Zu in tailings pore water.
		Iron (Fe)	kg	4.49	Calculated	Total iron in seepage. Assuming 2% net mobilisation of Fe in tailings pore water.
	Recovered Material	Water	tonnes	194.22	Calculated	Total water recoveries through return water from concentrate, tailings thickener and tailings storage facility
		Sulphide concentrate	tonnes	28.00	Calculated	Concentrate product
	Loss of material	Water	tonnes	39.11	Calculated	Total water losses from dissipated water streams (evaporated, seepage and entrainment water) and water in concentrate product.

[1] Further details regarding assumptions are provided on page 84-85

Table 17: Foreground process data arising from the management of 100 tonnes of solid tailings – Base case

Description			Units	Flows per 100 tonnes of solid tailings per day	Data source	Comments[1]
Inputs	Energy	Electricity	kJ	407 500	Calculated	Electricity from the grid used only for thickening and pumping tailings to tailings storage facility.
	Material	Tailings slurry (based on a solids content of 30% solids)	tonnes	333.3	Calculated	Feed tailings slurry. Calculation based on the addition of solids and water. Xanthate in slurry is assumed to be 1.5ppm NICNAS (2000)
Outputs	Waste streams	Tailings to disposal	tonnes	100	calculated	Assume 30 % entrainment of tailings water - 86.4 kg/100g of feed
		Water evaporation	tonnes	26.67	calculated	Assume 40% evaporation of tailings water
		seepage	tonnes	3.33	calculated	Assume 5% seepage of tailings water
	Emissions to ground water	Acid (H+)	kg	76	Calculated	Total acid (H+) in seepage. Calculations based on Net neutralisation potential (NNP) calculations.
		Sulphate (S)	kg	1072.0	Calculated	Total sulphate in seepage. Assuming 80% net mobilisation of S in tailings pore water.
		Calcium (Ca)	kg	92.6	Calculated	Total calcium in seepage. Assuming 60% net mobilisation of Ca in tailings pore water.
		Copper (Cu)	kg	0.2	Calculated	Total copper in seepage. Assuming 5% net mobilisation of Cu in tailings pore water.
		Zinc (Zn)	kg	11.1	Calculated	Total zinc in seepage. Assuming 60% net mobilisation of Zu in tailings pore water.
		Iron (Fe)	kg	49.7	Calculated	Total iron in seepage. Assuming 2% net mobilisation of Fe in tailings pore water.
	Recovered material	Water	tonnes	183.33	Calculated	Total water recoveries through return water from tailings thickener and TSF
	Loss of material	Water	tonnes	50.00	Calculated	Total water losses from dissipated water streams (evaporated, seepage and entrainment water) and water in concentrate product.

[1] Further details regarding assumptions are provided on page 84-85

The key assumptions underpinning the parameters in Tables 16 and 17 are as follows:

- **Tailings slurry feed (i.e. feed to the desulphurisation flotation)**

In line with data reported in the literature (refer to review), the feed tailings was assumed to have a solids content of 30% and a soluble xanthate concentration (residual from prior flotation steps) of 1.5ppm. This value is estimated based on an assumption made in the NICNAS report (2000), which was also found it to be consistent with values measured by Hawley (1977), who reported 0.2 to 1.2 mg/l of xanthate residue found in tailings.

- **Xanthate feed**

Xanthate is the major reagent and the main focus of the desulphurisation study assessment, therefore the amounts of other reagents used i.e. frother and modify are excluded in the study due to insufficient information on these reagents, as well as the relatively small quantities used. In the absence of available empirical data, and on the basis of discussions with in-house experts, 90 % of the xanthate used in the desulphurisation flotation process was assumed to be retained on the sulphide minerals collected as concentrate, when dried in smelters. The remaining 10% is assumed to report to the tailings storage facility as soluble xanthate.

- **Electricity consumption**

It was assumed that electricity consumption for the desulphurisation flotation process was similar to that used in a conventional flotation process of copper sulphide. In accordance with Figures published by Marsden et al, (2008), the total energy consumption for this process, which includes the flotation, solids handling and disposal operations is 16 300 kJ/tonne of ore (4.5kwh/tonne). This figure was similar to that obtained from in-house specialists. In the absence of available plant data, 25% (4 075 kJ/tonne of feed tailings) of this energy was attributed to dewatering and solids handling (base case scenario).

- **Solids content and water deportment**

In accordance with literature values, the solids content in the tailings thickener underflow was taken at 60% (Donoso et al., 2013) and that of the filtered concentrate at 90% (Bleiwas, 2012). Estimated water deportment during disposal is as follows: 40% evaporation; 30% entrainment; 10% seepage (Bleiwas, 2012). 20% of the slurry water is returned to the mill circuit after settling.

- **Long-term behaviour of tailings deposits**

As indicated in Chapter 3, subsection 3.2.1, that the waste deposit is considered as a ‘unit reactor’ that has its own emissions which includes residual processing reagents as well as

metals and salts which become mobilised during weathering of minerals. Only specific tailings components, which were copper and zinc, were taken into account due to lack of characterisation data for the tailings. In accordance with values predicted by Broadhurst (2007a) the extents of mobilisation under disposal conditions were estimated at 80% for S, 60% for Ca, 5% for Cu, 60% for Zn and 2% for Fe. These figures are based on a conventional porphyry-type tailings deposit with pore water in the pH range of 2-4 (Broadhurst, 2007a). No allowances were made for the effects of potentially lower or higher pH values in the base case or desulphurisation flotation scenarios respectively. Acid generation was calculated in accordance with the Maximum Potential Acidity (MPA) and Acid Neutralising Capacity (ANC) in accordance with the equation used for the Acid Base Accounting predictive test (Stewart et al., 2006). Acid neutralising capacity is assumed to be attributed to calcite only, whilst MPA is based on the total sulphur content. Two different sub-scenarios were created to account for xanthate behaviour in tailings deposit. In the first scenario (Scenario A), soluble xanthate (10% of feed) is assumed to deport to the groundwater without further decomposition. In scenario B, soluble xanthate is assumed to decompose in to carbon disulphide, alcohol and sodium hydroxide according to the reactions in equations 6 and 7 of Chapter 2 (subsection 2.1.1).

5.2.2 Background datasets

Background process data for both the base case and desulphurisation flotation management systems includes the production of South African electricity, which is coal based (Dick et al., 2012). In terms of material addition, the background system for the desulphurisation flotation includes xanthate production, where data was created in Chapter 4 of this thesis. Downstream treatment of the sulphide-rich stream was not included due to lack of adequate data and process information. Background data of relevant parameters for both scenarios are presented in Tables 18 and 19. The background data is essentially made up of both foreground elements (e.g. the quality of electricity consumed) and background elements (e.g. the emissions with electricity production).

Table 18: Background data arising from the management of 100 tonnes of solid tailings for the desulphurisation flotation treatment scenario

	Materials	Units	Background data		
			Xanthate (9 kg)	Electricity (1630000 kJ)	Total
Inputs	Water (process and cooling)	m^3	1.0E-02	6.0E-01	6.1E-01
	Fossil fuel (as hard coal @ mine)	kg	1.2E+00	1.7E+02	1.8E+02
	Sulphur (S)	kg	1.4E-04	1.7E-06	1.4E-04
	Zinc (Zn)	kg	8.9E-04	5.1E-04	1.4E-03
	Copper (Cu)	kg	2.0E-04	6.5E-05	2.7E-04
	Iron (Fe)	kg	4.9E-02	7.5E-02	1.2E-01
Outputs	Acid (H+)	kg	0	0	0
	Sulphur (as sulphate)	kg	3.7E-01	2.0E+01	2.0E+01
	Zinc (Zn)	kg	6.7E-04	2.8E-02	2.9E-02
	Copper (Cu)	kg	1.1E-04	3.0E-03	3.1E-03
	Iron (Fe)	kg	1.2E-02	4.5E-01	4.6E-01
	Manganese (Mn)	kg	4.6E-03	2.0E-01	2.0E-01
	Xanthate	kg	0	0	0
	Sulphur dioxide (SO_2)	kg	3.9E-01	3.6E+00	4.0E+00
	Carbon dioxide (CO_2)	kg	1.6E+01	5.5E+02	5.6E+02
	Solid emissions (final waste flows)	kg	2.8E-01	5.0E+01	5.0E+01

Table 19: Background data arising from the management of 100 tonnes of solid tailings for the base case scenario

	Materials	Units	Background data
			Electricity (407 500 kJ)
Inputs	Water (process and cooling)	m^3	1.5E-01
	Fossil fuel (as hard coal @ mine)	kg	4.3E+01
	Sulphur (S)	kg	4.3E-07
	Zinc (Zn)	kg	1.3E-04
	Copper (Cu)	kg	1.6E-05
	Iron (Fe)	kg	1.9E-02
Outputs	Acid (H+)	kg	0
	Sulphur (as sulphate)	kg	4.9E+00
	Zinc (Zn)	kg	7.0E-03
	Copper (Cu)	kg	7.4E-04
	Iron (Fe)	kg	1.1E-01
	Manganese (Mn)	kg	4.8E-02
	Xanthate	kg	0
	Sulphur dioxide (SO_2)	kg	8.9E-01
	Carbon dioxide (CO_2)	kg	1.4E+02
	Solid emissions (final waste flows)	kg	1.2E+01

Based on the management of 100 tonnes of solid tailings, background processes for the desulphurisation flotation treatment process involves the production of 9 kg of xanthate and 1 630 000 kJ of electricity as system inputs (Table 18). The production of the coal-based electricity consumes less materials (sulphur, zinc and copper), however it has higher emissions to water (sulphur as sulphate, zinc, copper and iron), compared to the production of xanthate. This process also results in higher SO_2 and CO_2 emissions, than the production of xanthate, which is largely attributed to the use of fossil fuel for electricity production. Background data for the base case scenario only involves the production of electricity (407 500 kJ), which is predicted to be significantly lower (25%) than that for the desulphurisation flotation scenario (Table 19). This results in less consumption of input materials used (water, sulphur, zinc, copper and iron), than the desulphurisation flotation treatment scenario. The lower electricity use also results in less emissions to water (sulphur as sulphate, zinc, copper and iron) and air (SO_2 and CO_2).

5.2.3 LCI analysis

Table 20 summarises the key LCI parameters derived for the two tailings treatment scenarios on the basis of the reference feed rate (100 tonnes/day of solids).

Table 20: Summary of key LCI parameters arising from the management of 100 tonnes of solid tailings for the two tailings treatment scenarios

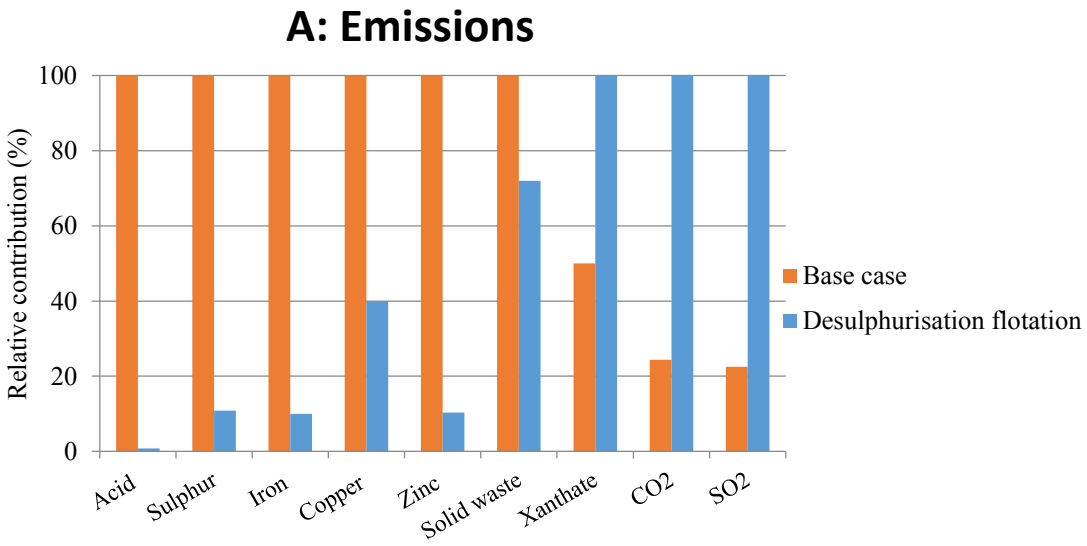
Description			Units	Flows per 100 tonnes of solid tailings per day		Relative contribution of foreground system (% of total)	
				Desulphurisation flotation scenario	Base case scenario	Desulphurisation flotation scenario	Base case scenario
Inputs	Energy	Electricity	kJ	1 630 000	407500	100%	100%
	Material	Tailings slurry	tonnes	333.3	333.3	100%	100%
		Water in tailings slurry	tonnes	233.3	233.3	100%	100%
		Xanthate feed	kg	9.00	-	100%	100%
Outputs	Emissions to ground water (Seepage)	Acid (H+)	kg	0.59	76.0	100%	100%
		Sulphur (S)	kg	116.35	1076.87	82.9%	99.5%
		Copper (Cu)	kg	0.08	0.2	97%	99.6%
		Zinc (Zn)	kg	1.14	11.1	97.5%	99.9%
		Iron (Fe)	kg	4.95	49.82	90.6%	99.8%
		Xanthate	kg	0.02	0.01	100%	100%
	Emissions to air	Carbon dioxide	kg	562.50	137	0%	0%
		Sulphur dioxide	kg	3.96	0.89	0%	0%
	Emissions to land	Unreactive solid tailings	tonnes	72	100	100%	100%
	Non-recoverable resources (Losses)	Water	m^3	39.1[1]	50.2[2]	98%	99.7%
		Sulphur	tonnes	2.9	11.4	100%	100%
		Carbon	kg	152.7	38.2	100%	100%
		Iron	tonnes	0.75	8.1	100%	100%
		Copper	tonnes	0.01	0.03	100%	100%
		Zinc	tonnes	0.01	0.13	100%	100%

[1] Dissipative water lost as evaporation, seepage, entrainment and dewatered concentrate product; [2] dissipative water lost as evaporation, seepage and entrainment.

A comparison of the LCI data for the two tailings treatment processes indicates that the desulphurisation flotation process consumes more carbon than the base case scenario, and results in higher emissions of carbon dioxide (76% more), sulphur dioxide (78% more) and xanthate (50% more) to the environment.

However, it also results in a considerable decrease in the aqueous emissions of acid (99% less), sulphur, as sulphate (89% less) and metals [copper (60% less); zinc (90% less); iron (90% less)], whilst simultaneously enhancing the potential to recover valuable resources, including water and metal values (Cu, Zn and Fe) from the tailings (as seen in Table 18). The relative emissions and resources losses are illustrated diagrammatically in Figures 33A and 33B respectively.

Further analysis of the LCI data indicated that in both cases, dissipative water losses are attributed largely to evaporation and seepage within the sulphide tailings impoundment, both of which are reduced in the case where desulphurisation flotation is conducted prior to disposal. Losses of soluble sulphur and metals can also be attributed largely to the deposition of tailings in solid waste impoundments, with all components in the solid waste streams being considered as resource 'losses' as they are no longer available for utilisation, regardless of their extent of mobilisation under disposal conditions. Losses of carbon can be attributed almost exclusively to emissions of carbon dioxide (CO_2) during fossil-fuel based electricity production, whilst emissions of sulphur dioxide (SO_2) during fossil-fuel based electricity production also make a significant contribution to net sulphur losses for the desulphurisation flotation tailings treatment scenario (82% of total). The higher electricity consumption by the desulphurisation flotation process results in higher net carbon consumption and CO_2 emissions relative to the base case scenario.



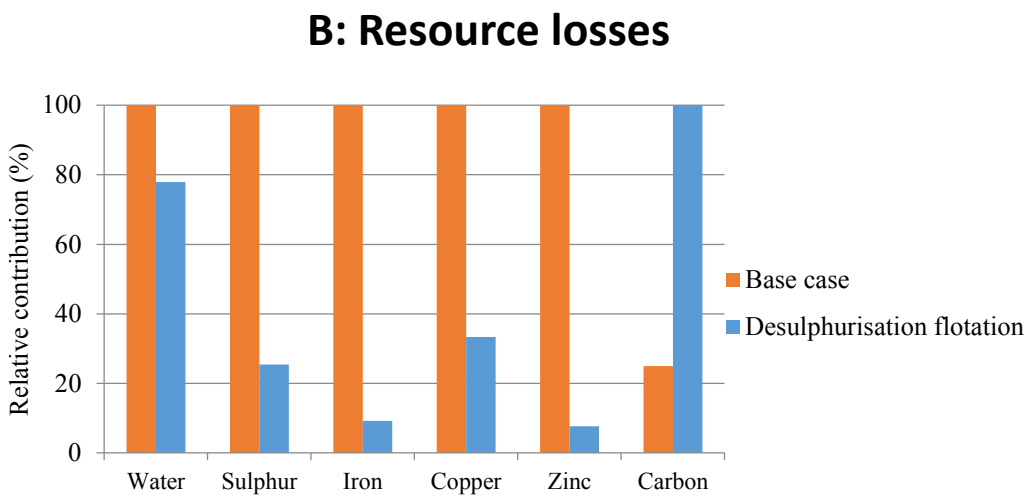


Figure 33: Relative environmental emissions (A) and resource losses (B) arising from the management of 100 tonnes of solid tailings for the two tailings treatment scenarios

5.3 Life cycle impact assessment (LCIA)

This section presents and discusses the results of the life cycle impact assessment modelling. As discussed previously the USEtox method was used to assess human and ecotoxicity impacts, taking into account two scenarios for the behaviourof xanthate. The ReCiPe method was used to model climate change, fossil fuel depletion, terrestrial acidification, urban land occupation and natural land transformation impacts, as well as human and ecotoxicity impacts for the case where xanthate does not decompose (scenario A).

5.3.1 USEtox method for toxicity analysis

Scenario A: Soluble xanthate deports to seepage without decomposition

On the basis of available data, LCIA modelling with USEtox indicates that desulphurisation flotation results in a considerable reduction (more than 89%) in both ecotoxicity and human toxicity impacts (Figure 34).

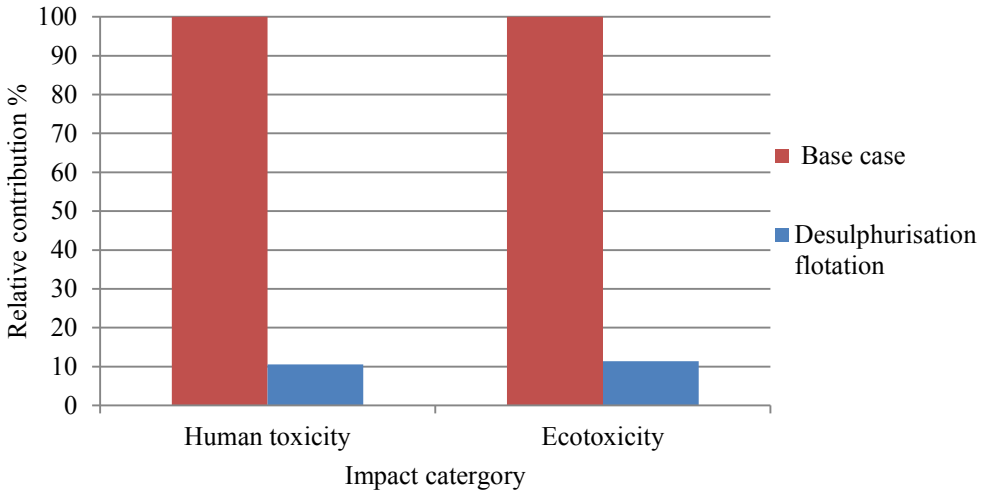


Figure 34: Relative human and ecotoxicity impacts arising from the management of 100 tonnes of solid tailings for the two tailings treatment scenarios : USEtox method without xanthate decomposition (scenario A)

The tailings treatment process accounts for the majority of the human and ecotoxicity impacts in both cases, with electricity production accounting for 5% of human and 3% of ecotoxicity in the case of the desulphurisation flotation management scenario.

Figure 35 and 36 shows the relevant substances contributing to human toxicity and ecotoxicity respectively, for both scenarios. These impacts are measured in comparative toxic units (human toxicity) (CTUh) and comparative toxic units (ecotoxicity) (CTUe) equivalent per management of 100 tonnes of solids tailings.

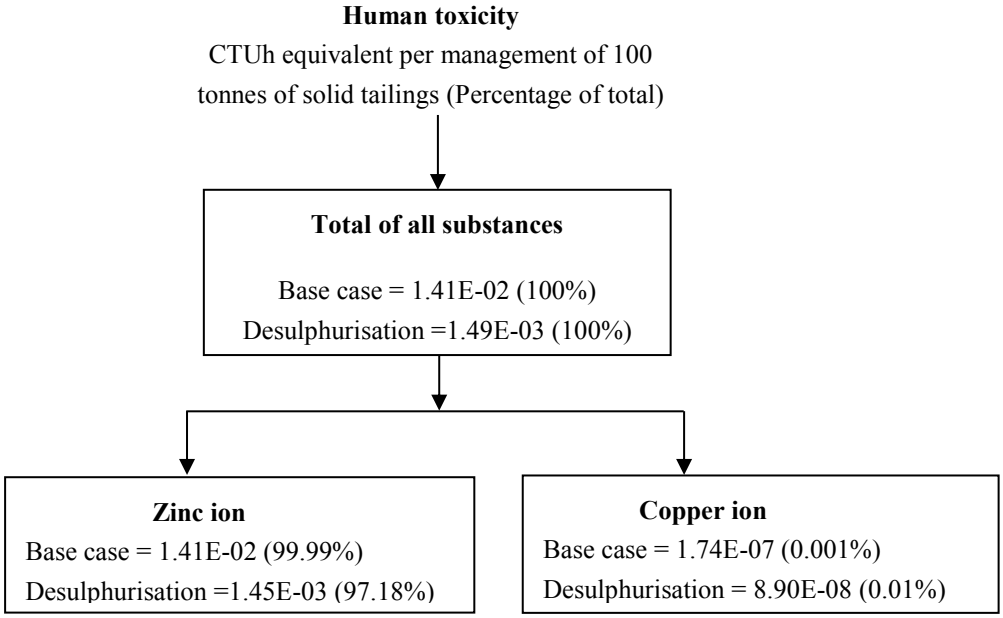


Figure 35: Contributions of emissions to human toxicity impact category arising from the management of 100 tonnes of solid tailings for the two tailings treatment scenarios: USEtox method without xanthate decomposition (scenario A)

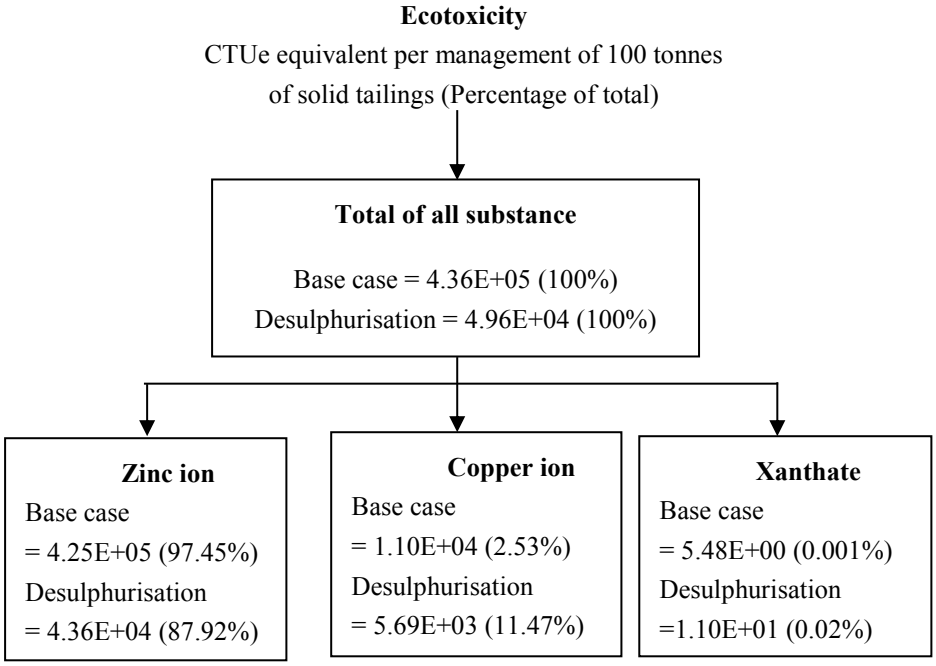


Figure 36: Contributions of emissions to ecotoxicity impact category arising from the management of 100 tonnes of solid tailings for the two tailings treatment scenarios (scenario A)

The LCA results indicate that for both scenarios, the human toxicity (Figure 35) and ecotoxicity (Figure 36) impacts can be mainly attributed to zinc emissions (88-100% of total impacts). Copper emissions make a small contribution to ecotoxicity impacts (3-11.5%) but a negligible contribution to human toxicity impacts (< 0.01%). The USEtox model also predicts a negligible contribution to ecotoxicity impacts from xanthate emissions (< 0.02%), while human toxicity impact is not characterised for xanthate emissions. This can be attributed to both the relatively low net emissions (Table 20) and toxicity characterisation factors for xanthate relative to zinc (Appendix J). It should, however, be noted that only the mobilisation of Cu, Fe, Zn and Ca were considered due to lack of availability of data on tailings composition. Other elements that could be a problem are Al, Mn, Ni, Co and As as previously mentioned from the literature reviewed. Furthmore, the impact of emissions of acid, iron, calcium and sulphate emissions could not be assessed as LCIA toxicity models views salinity as an indicator that carries dissolved species such as metals, therefore its impacts are not assessed. However as highlighted previously in the literature reviewed, salinity impacts can lead to human and ecotoxic effects and also have adverse effect on the quality of water and water sources.

Scenario B: Soluble xanthate decomposition to carbon disulphide, alcohol and sodium hydroxide

As discussed in the literature review, xanthate may decompose in the tailings dam. When considering the decomposition products of soluble xanthate (carbon disulphide, alcohol and

sodium hydroxide) for the disposal of tailings, the LCIA modelling indicates once again that desulphurisation flotation results in a considerable reduction (more than 89%) in both ecotoxicity and human toxicity impacts (Figure 37). The results are similar to scenario A: soluble xanthate in seepage, as seen in the previous subsection.

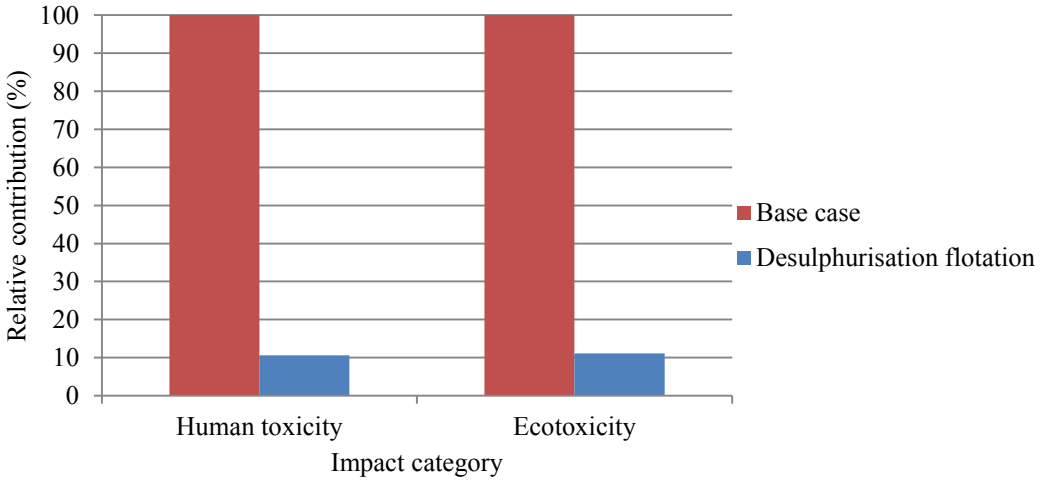


Figure 37: Relative human and ecotoxicity impacts arising from the management of 100 tonnes of solid tailings for the two tailings treatment scenarios (scenario B)

Figure 38 and 39 shows the relevant substances contributing to human toxicity and ecotoxicity respectively, for both scenarios. These impacts are measured in comparative toxic units (human toxicity) (CTUh) and comparative toxic units (ecotoxicity) (CTUe) equivalent per management of 100 tonnes of solids tailings.

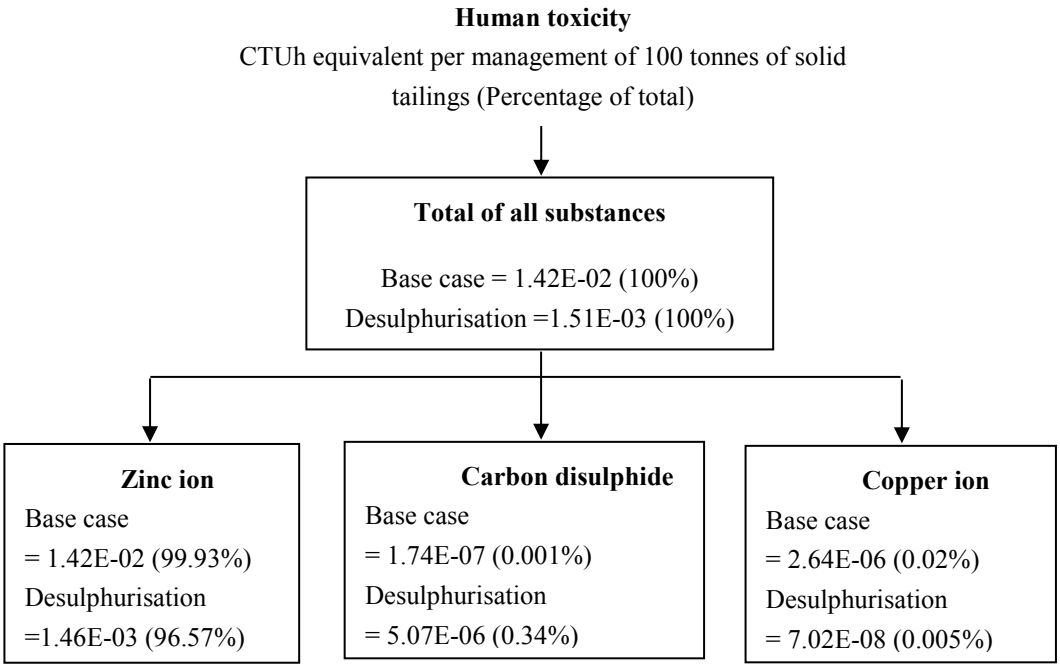


Figure 38: Contributions of emissions to human toxicity impact category arising from the management of 100 tonnes of solid tailings for the two tailings treatment scenarios (scenario B)

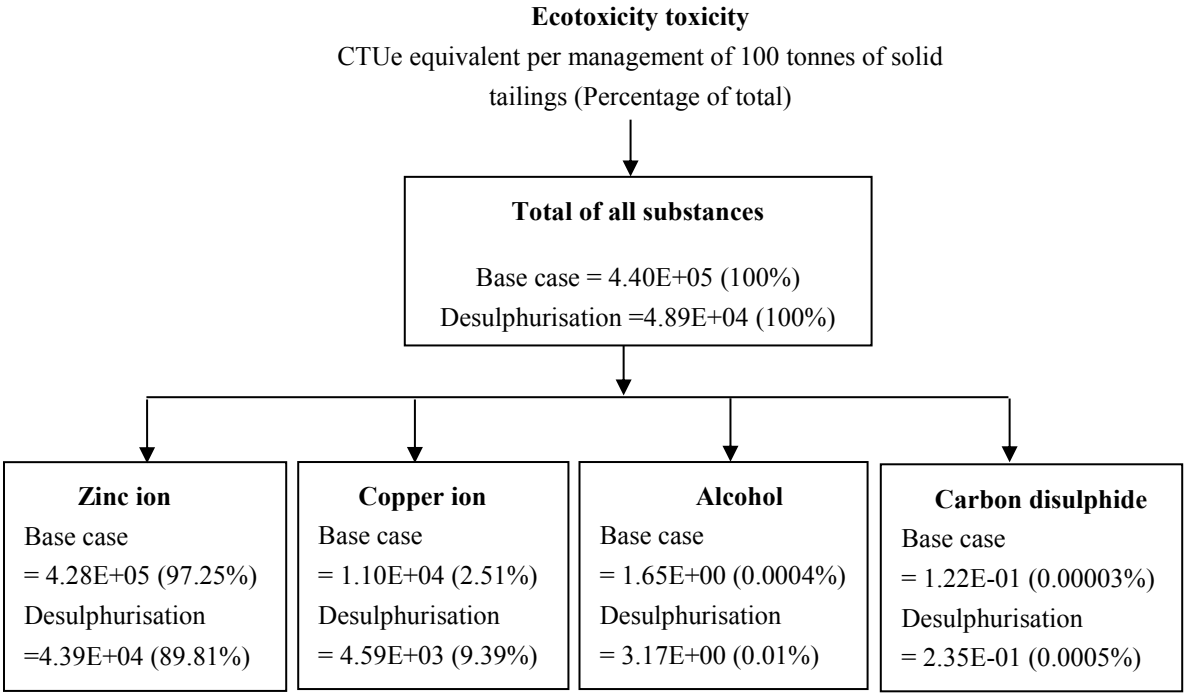


Figure 39: Contributions of emissions to ecotoxicity impact category arising from the management of 100 tonnes of solid tailings for the two tailings treatment scenarios (scenario B)

Results indicate that for both scenarios, the human toxicity (Figure 38) and ecotoxicity (Figure 39) impacts can be mainly attributed to zinc emissions (90-100% of total impacts. Copper emissions make a small contribution to ecotoxicity impacts (2.5-9%) but a negligible contribution to human toxicity impacts (< 0.02%). USEtox method predicts a negligible contribution to human toxicity and ecotoxicity impacts of xanthate decomposition products emissions, carbon disulphide (< 0.02%) and alcohol (<0.01%) which is only characterised for ecotoxicity impact. This can be attributed to both the relatively low emissions (Appendix H, Table H 1) and toxicity characterisation factors relative to the metals (Zn and Cu) (Appendix J). The impact of sodium hydroxide emissions could not be assessed due to the absence of characterisation factors for this substance, as well as other metals – both considered and not considered.

5.3.2 ReCiPe method analysis

Based on the current assumptions in terms of energy consumption, LCIA modelling results, using ReCiPe method (Figure 40) indicate that the desulphurisation flotation tailings management scenario results in significantly higher climate change (76%), fossil fuel depletion (77%) and terrestrial acidification (77%) impacts than the base case scenario. However, it results in lower urban land occupation (27%) and natural land transformation (26%), as well as human toxicity (50%) and ecotoxicity (85%) impacts.

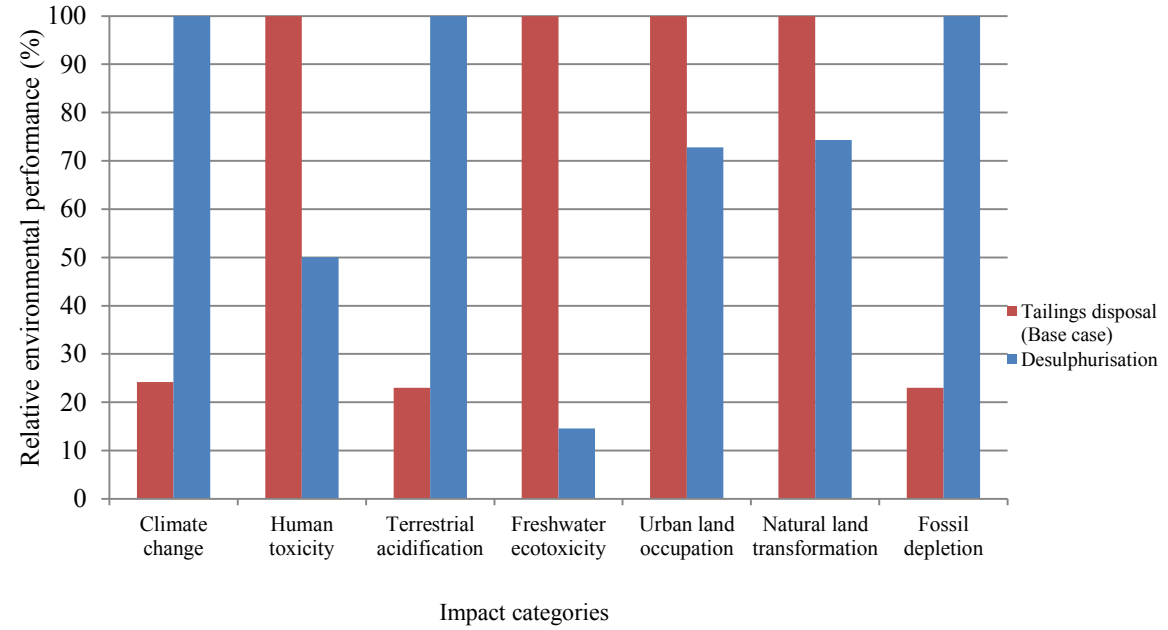


Figure 40: Relative environmental performances arising from the management of 100 tonnes of solid tailings for the two compared scenarios using ReCiPe method

Further analysis of the relative process contributions of the scenarios to the impact categories are shown (Figures 41 and 42) and discussed below. Detailed results are presented in Appendix I, Table I3.

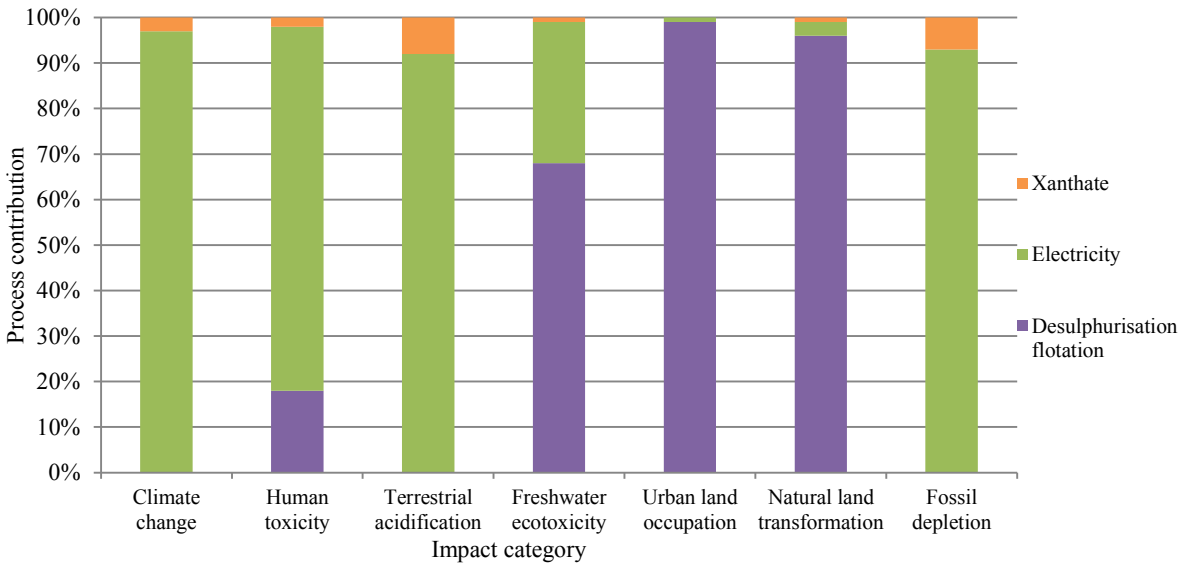


Figure 41: Material and process contributions to the potential environmental impacts arising from the management of 100 tonnes of solid tailings via the desulphurisation flotation scenario

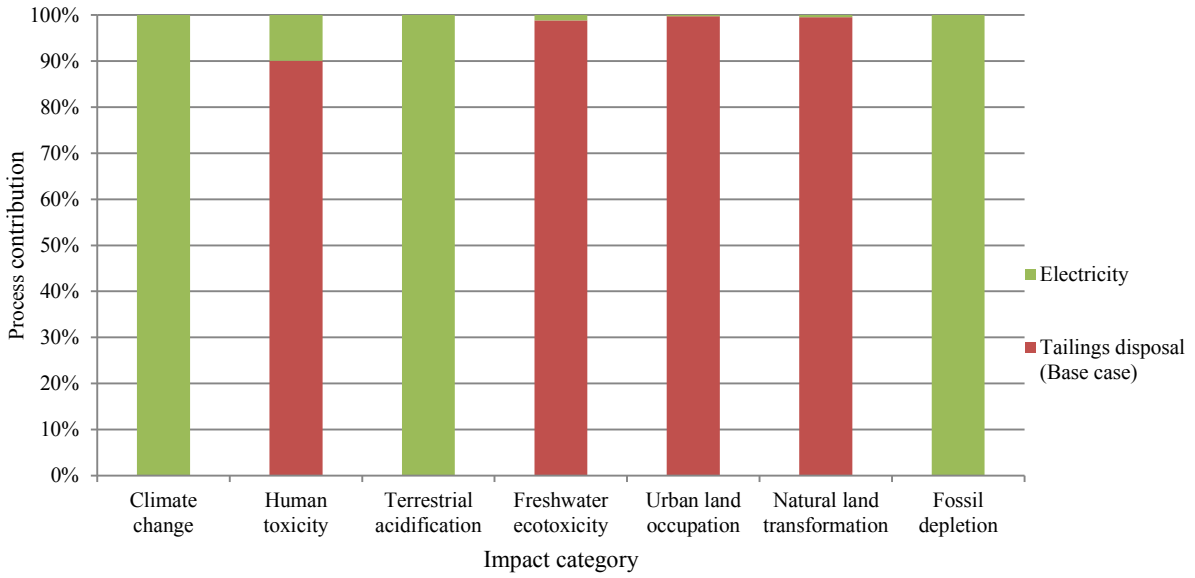


Figure 42: Material and process contributions to the potential environmental impacts arising from the management of 100 tonnes of solid tailings via the base case scenario

- **Climate change, fossil fuel depletion and terrestrial acidification**

Analysis of the relative contributions of the processes in the case of the desulphurisation flotation treatment scenario (Figure 41) indicates that climate change, fossil fuel depletion and terrestrial acidification impacts can be largely attributed to the production of fossil-fuel based electricity (>90% in the case of the desulphurisation flotation treatment scenario, and 100% in the case of the base case scenario). The production of xanthate makes a small contribution to climate change (3%), fossil fuel depletion (7%) and terrestrial acidification (8%).

- **Urban land occupation and natural land transformation**

These impacts can be attributed largely to the land disposal of tailings (foreground process) for both management scenarios. As illustrated in Figure 40, the desulphurisation flotation treatment scenario results in lower urban land occupation and natural land transformation impacts than those for the base case scenario. This can be attributed largely to the smaller quantities of land-disposed tailings in the case of the desulphurisation flotation treatment process.

- **Human and ecotoxicity**

The human toxicity impact in the case of the base case scenario is largely attributed by the treatment scenario itself (Figure 42). However, in the case of the desulphurisation flotation scenario (Figure 41), LCIA results indicate that this impact category is largely dominated by

the production of fossil-fuel based electricity (80%), while the treatment scenario itself has a lower contribution (18%). This is in contradiction to the results obtained using USEtox method in subsection 5.3.1(scenario A), which indicated that the tailings treatment process accounts for the majority of the human toxicity impacts, with electricity production accounting for only 5%. The freshwater ecotoxicity impact is largely dominated by the treatment scenarios, contributing 99% in the case of the base case and 68% in the case of the desulphurisation flotation scenario.

Further analysis indicates that for both scenarios, the ecotoxicity impacts (Figure 44) can be mainly attributed to zinc emissions (62.9-98% of total impacts). However, in the case of human toxicity impacts (Figure 43), ReCiPe model predicts a relatively high contribution of manganese emissions (66% of total impact) for the desulphurisation flotation scenario, while the USEtox model does not consider manganese. Although the presence and mobilisation of manganese in the tailings deposit was not included in the study, its emission can be attributed to fossil fuel based electricity production and the relatively high toxicity characterisation factors for manganese relative to zinc (Appendix J). This discrepancy between the two methods used to analyse the toxicity impacts, emphasises the high uncertainty in characterising factors of metals in LCIA methods, as previously discussed in the literature review. USEtox method are marked 'interim', which means metal characterisation factors may be used, but with great caution due to their large uncertainty. The impact of emissions of copper and xanthate could not be assessed due to the absence of characterisation factors for these substances.

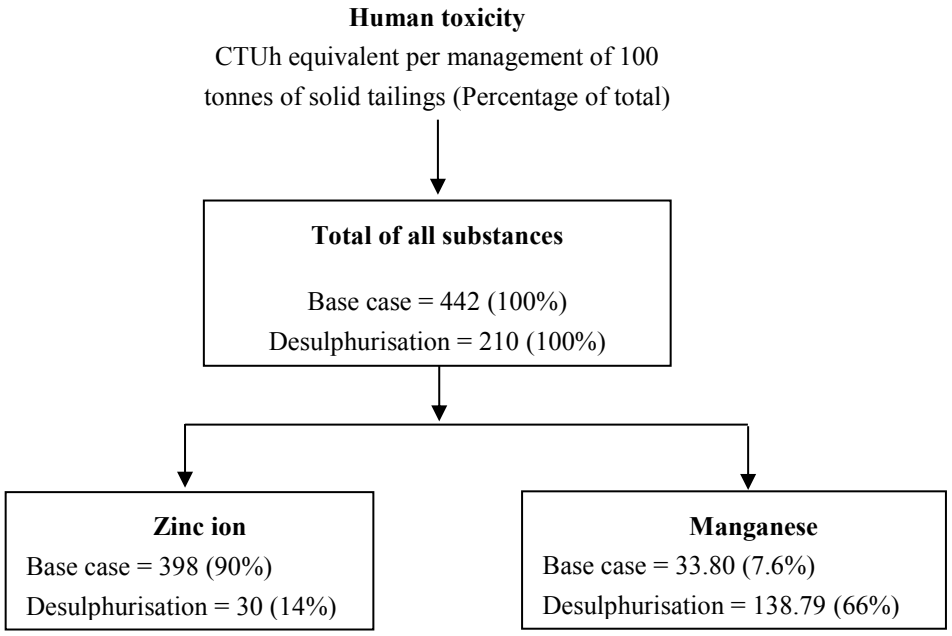


Figure 43: Contributions of emissions to human toxicity impact category arising from the management of 100 tonnes of solid tailings for the two tailings treatment scenarios

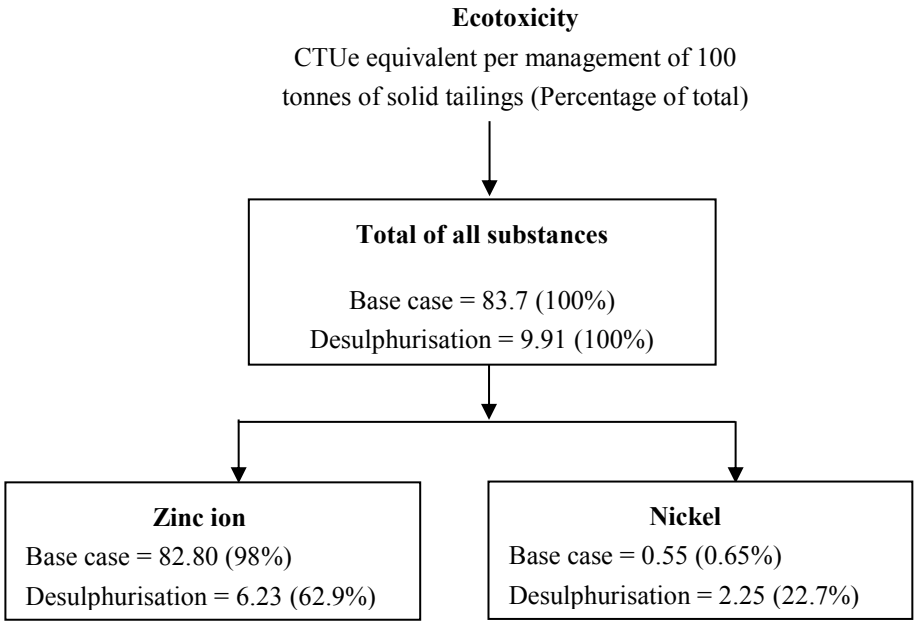


Figure 44: Contributions of emissions to freshwater ecotoxicity impact category arising from the management of 100 tonnes of solid tailings for the two tailings treatment scenarios

5.4 Sensitivity Anaysis: Desulphurisation Flotation Management Scenario 1

A sensitivity analysis is used to analyse the parameters that were chosen on the basis of their relevance and/ or level of uncertainty and to evaluate the extent to which the results of the study were influenced by these variations and assumptions made.

The parameters chosen using sensitivity analysis were: energy consumption, ore mineralogy, mobilisation of metals as well as xanthate deportment to the tailings storage facility. The sensitivity analysis was performed by varying the identified parameters to observe the effects they had on the impact categories. The results are presented graphically and show the percentage change in impact category as a function of a percentage in the parameter. Only the impact categories with significant changes are shown. A negative change indicates reduced contributions to an impact category, and thus reflects the potential for an improved environmental profile of the treatment and management of tailings. Detailed results of the varied parameters are presented in Appendix K.

5.4.1 Effect of electricity consumption

The LCIA modelling results indicated that the climate change, fossil fuel depletion and terrestrial acidification impacts of both treatment processes can be largely attributed to the consumption of fossil fuel based electricity. In the absence of empirical data on electricity consumption, generic data as derived from the open literature was used (see Table 2). This

key model input parameter is thus characterised by a probability of overestimation, as the conventional flotation operations, on which this data was based, involve extensive regrinding circuits, which can be highly energy intensive. The sensitivity analysis results for the desulphurisation flotation process (Figure 45) confirm the significance of electricity consumption in terms of environmental performance, with a 40% decrease in electricity consumption (equivalent to 2.7 kWh/tonne) resulting in a decrease of 39% in climate change and 37% in both fossil fuel depletion and terrestrial acidification impacts.

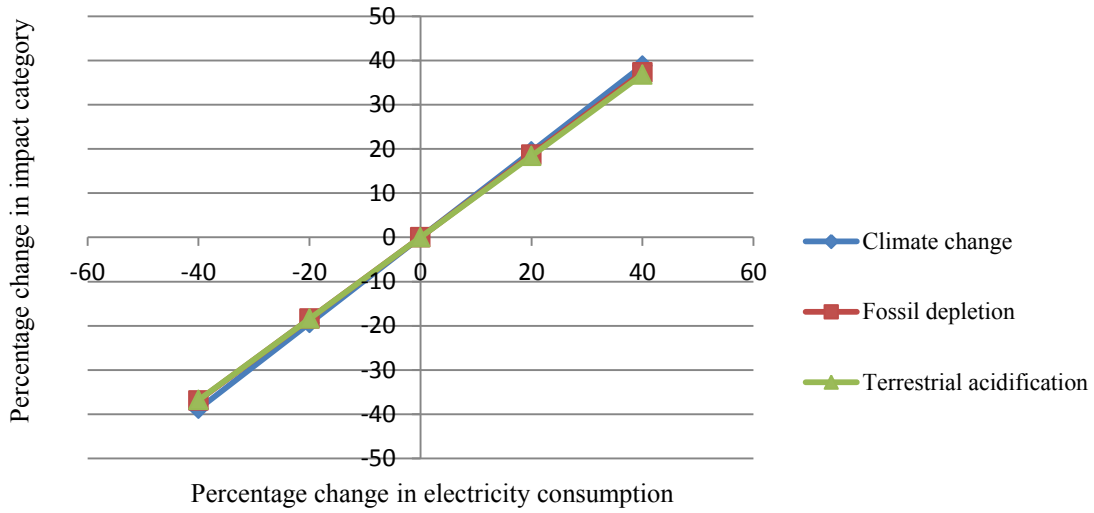


Figure 45: Sensitivity analysis of impacts to energy consumed during the treatment of 100 tonnes of solid tailings using the desulphurization process.

5.4.2 Effect of zinc and copper in the tailings

- *Zinc*

LCIA modelling using both USEtox and ReCiPe indicated that zinc emissions are the primary contributor to human toxicity and ecotoxicity for both tailings treatment scenarios. Ultimately the environment emissions of zinc for any given tailings treatment process will be dependent on the concentration of zinc in the feed tailings and the extent to which zinc is mobilised under disposal conditions. Zinc concentration in the feed tailings of the base metal tailings sample used for this study was 0.13%, which is significantly higher than the concentrations of 0.01–0.06% reported for a typical porphyry-type copper sulphide tailings stream (Broadhurst et al., 2007b). When investigating the sensitivity of human and ecotoxicity to total zinc concentration in the feed tailings, by means of USEtox for scenario A (assuming no decomposition of xanthate). As expected, the sensitivity results (Figure 46) show that the human and ecotoxicity impacts for both tailings treatment scenarios are highly sensitive to the zinc concentration in the feed tailings. For the desulphurisation flotation

process a decrease in zinc concentration in the feed tailings from 0.13% to 0.01% (90% reduction) results in a 91% and 82% decrease in human toxicity and ecotoxicity impacts respectively.

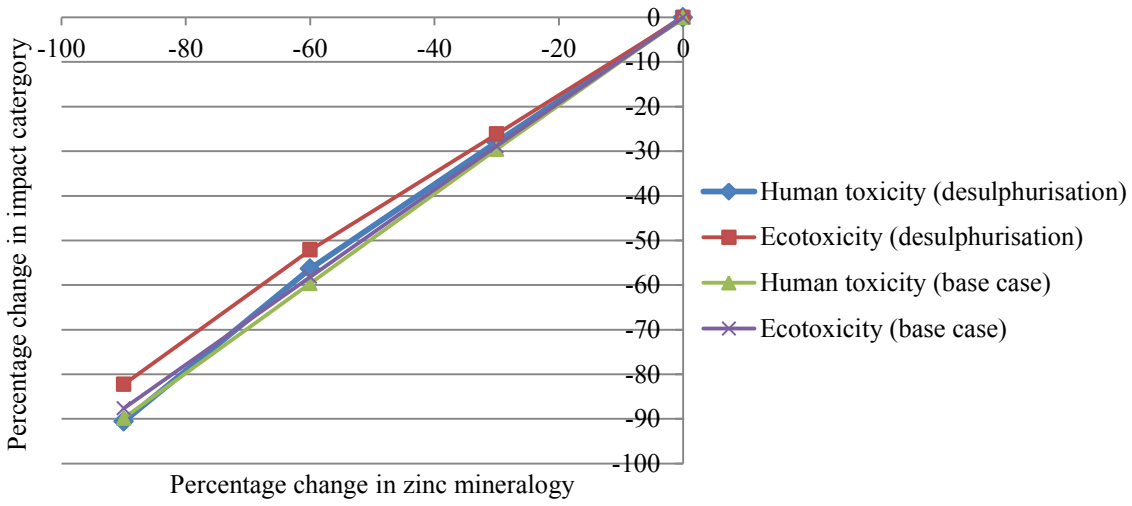


Figure 46: Sensitivity analysis of toxicity impacts to total zinc concentration in the feed tailings, during the treatment of 100 tonnes of solid tailings

- *Copper*

The LCIA modelling results in scenario A (Figures 38 and 39) indicated that copper makes a small to negligible contribution to human and ecotoxicity impacts for both tailings treatment scenarios. However, the copper concentration in the base metal feed tailings sample used in this case study was relatively low (0.03%) in comparison to the values of 0.08-0.17% reported for a typical porphyry-type copper sulfide tailings (Broadhurst and Petrie, 2010). As expected, the results of the sensitivity analysis (Figure 47) indicate that the ecotoxicity and , in particular, the human toxicity impacts are considerably less sensitive to copper than to zinc feed concentrations. An increase in the copper feed concentration from 0.03% to 0.17% (467% increase) results in an increase in the ecotoxicity impact of 44% in the case of the desulphurisation flotation process, and has a negligible effect on human toxicity.

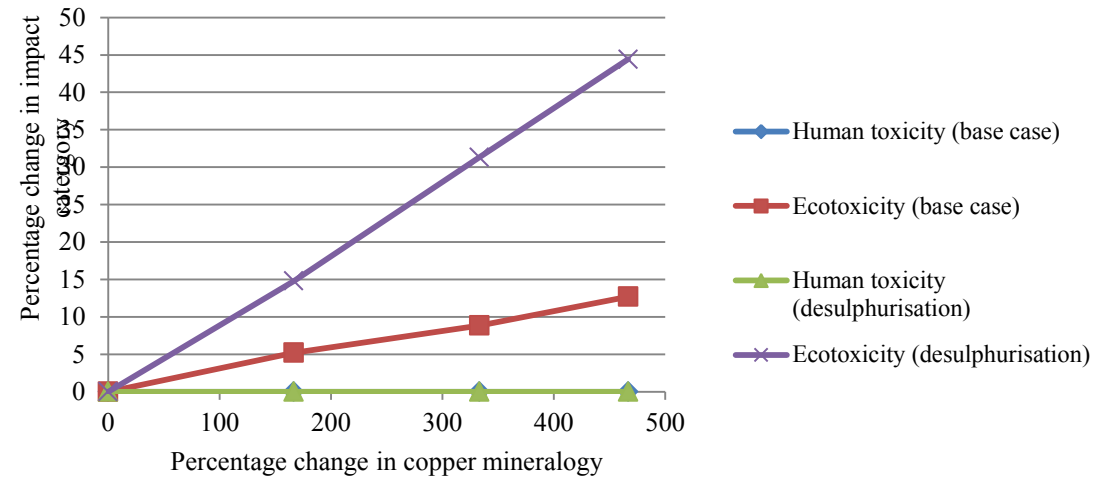


Figure 47: Sensitivity analysis of toxicity impacts to feed copper concentration, during the treatment of 100 tonnes of solid tailings

5.4.3 Effect of zinc and copper mobility

- *Zinc*

Similar to zinc concentration in the feed tailings, the extent of zinc mobilisation under disposal conditions has a significant effect on human toxicity and ecotoxicity (Figure 48). For the desulphurisation flotation process, a decrease in the predicted extent of Zn mobilisation from 60% (after Broadhurst and Petrie, 2010) to 30% (i.e. a 50% reduction), results in a 52% and 47% decrease in human toxicity and ecotoxicity impacts respectively. Increasing the extent of Zn mobilisation to 90% (i.e. a 50% increase) results in a 43% and 39% increase in human toxicity and ecotoxicity respectively.

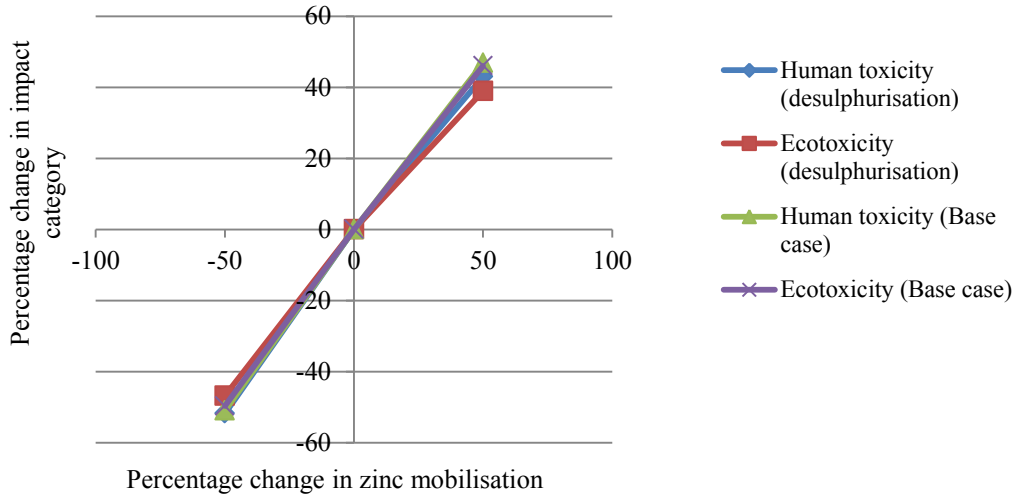


Figure 48: Sensitivity analysis of toxicity impacts to the extent of zinc mobilisation during disposal, during the treatment of 100 tonnes of solid tailings

Assuming that the extend of mobilisation of zinc for the desulphurisation tailings disposal scenario is less (45% mobilisation) than the assumed 60% because of neutral to weakly alkaline pH values (7-9) experienced, whereby zinc tends to mobilise less at this condition and forms carbonate precipitate. The mobilisation of zinc for the base case is kept constant at the assumed 60% mobilisation because of the lower acidic condition. As expected, sensitivity results in a 26% and 23% decrease in human toxicity and ecotoxicity impacts respectively (Figure 49), and no change is experienced for the base case tailings scenario. These results emphasize the potential benefits of the desulphurisation process which is expected to render the tailings neutral and prevent or significantly reduce metal mobilization as compared to non desulphurised tailings (Base case scenario).

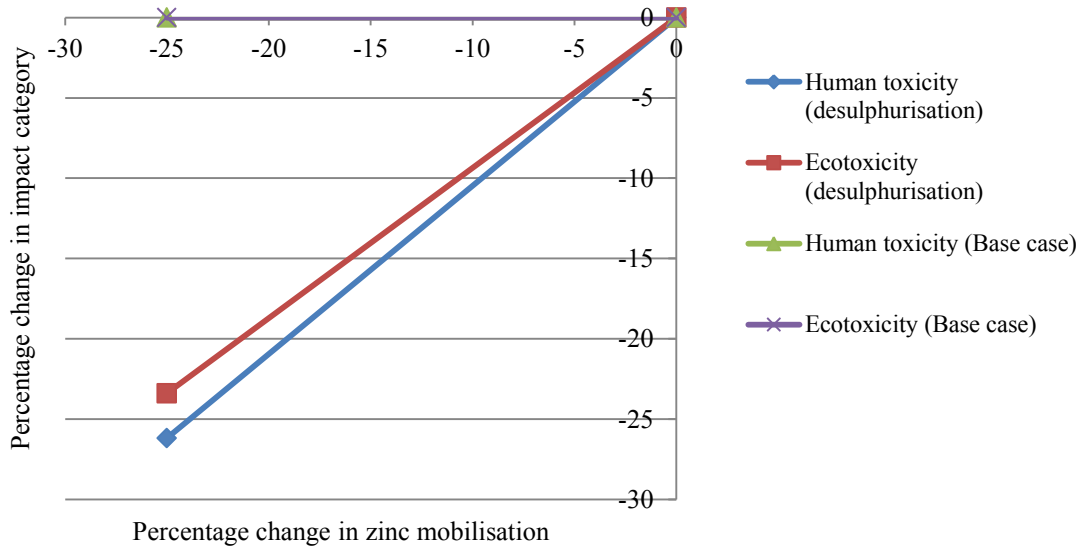


Figure 49: Sensitivity analysis of toxicity impacts to the extent of zinc mobilisation at weakly alkaline pH values, during the treatment of 100 tonnes of solid tailings

- *Copper*

Copper is assumed to have very low net mobility (5%). The predicted mobilisation from literature is < 10% (Broadhurst, 2007a). The sensitivity analysis (Figure 50) indicate that an increase of 100% (10% net copper mobilisation) will result in an increase in ecotoxicity impacts of 11% for the desulphurisation flotation process, and no impact change on human toxicity. Decreasing the copper net mobilisation by 80% (1% net copper mobilisation), results in an ecotoxicity impact improvement of 9% for the desulphurisation flotation process.

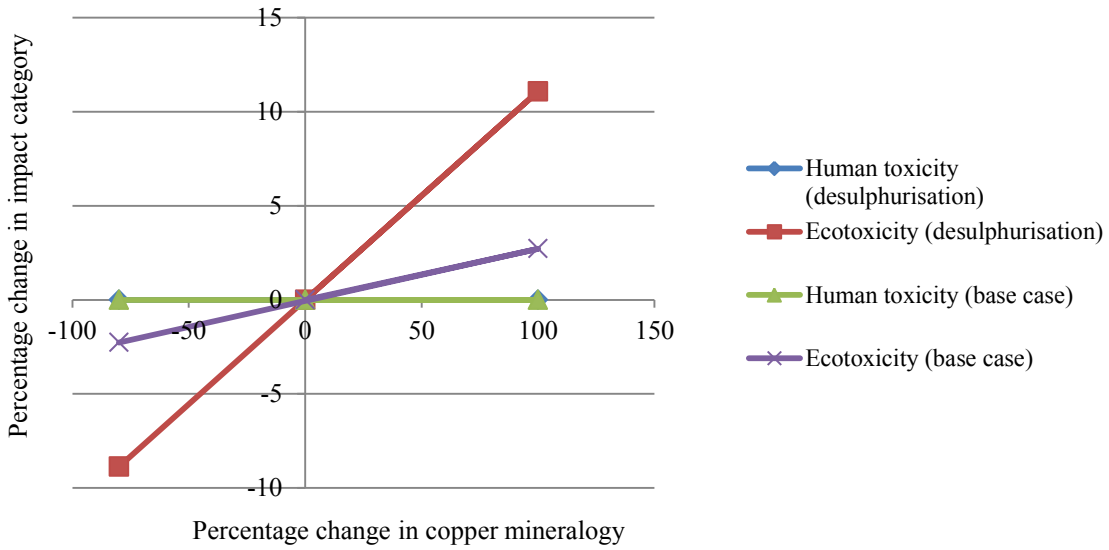


Figure 50: Sensitivity analysis of toxicity impact to extent of copper mobilisation during disposal, during the treatment of 100 tonnes of solid tailings

5.4.4 Effect of xanthate deportment

A sensitivity analysis is performed to explore the potential environmental effects of decreasing and increasing the assumed remaining 10% deportment of xanthate to the tailings storage facility for the desulphurisation tailings scenario. Results are presented in Figure 51. A decrease of 50% (5% deportment) or an increase of 100% (20% deportment) of the soluble xanthate reporting to the tailings storage facility, results in no change (0%) in human and ecotoxicity impact categories.

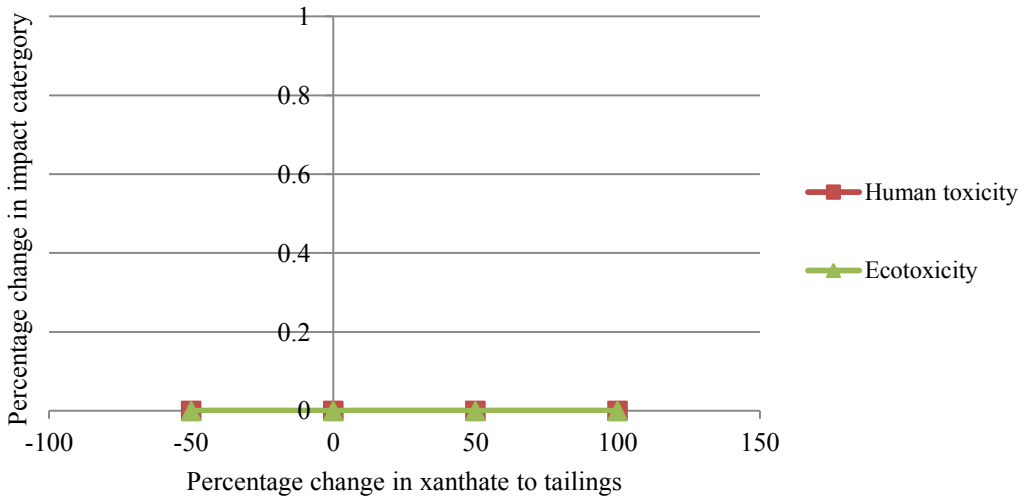


Figure 51: Sensitivity analysis of toxicity impacts to deportment of soluble xanthate during desulphurisation tailings disposal, during the treatment of 100 tonnes of solid tailings

5.4.5 Summary of sensitivity analysis

Sensitivity analysis results have shown that changes in key parameters (electricity, ore mineralogy and mobilisation of metals) can greatly affect the environmental performance of the two scenarios. In the case of the desulphurisation flotation scenario, significant environmental improvements are mostly observed with a decrease in: (1) electricity consumption, a 40% reduction of which results in a 39% decrease in climate change impacts and a 37% in both terrestrial acidification and fossil depletion impacts; (2) zinc feed concentration in tailings, with a 90% reduction resulting in a 91% and 82% decrease in human toxicity and ecotoxicity impacts respectively; (3) zinc mobilisation, with a 50% reduction resulting in a 52% and 47% decrease in human toxicity and ecotoxicity impacts respectively.

5.5 Limitations of the study

Limitations of this study pertain to the quality of the input data (in terms of both availability and certainty), the impact categories considered, as well as the LCIA modelling capabilities.

(a) Input data availability and quality

As indicated in Tables 18 and 19, the life cycle inventory was based on a number of assumptions due to the lack of currently available empirical data to adequately describe the treatment scenarios. This relates in particular to the consumption of electricity and the mobilisation of zinc under disposal conditions, both which have been shown to have a significant effect on the environmental performance.

Another key uncertainly related to the deportment and behaviour of xanthate salts during desulphurisation flotation and tailings disposal. The literature reviewed indicated that xanthate is relatively unstable and may decompose fairly rapidly to form toxic by-products such as carbon disulphide (NICNAS, 1995). Whilst, in a more recent study by Rostad et al. (2011), only the xanthate degradation products ispropyl xanthyl sulfonate and isopropyl xanthyl thiosulfonate were detected in tailing pond water samples. However, when considering the decomposition products of soluble xanthate (carbon disulphide, alcohol and sodium hydroxide) for the disposal of tailings, as modelled in subsection 5.3.1, Scenario B, the USEtox model indicated negligible toxicity impacts from xanthate and its decomposition products at the predicted residual concentration levels.

It should be noted that mining operations throughout the world have different and specific flotation characteristics and handling of disposed tailings. For example, depending on the

weather conditions of where the mine is situated, evaporation of water in the tailings storage facility can vary for a specific mine. Applying these results into different contexts and mining operations could lead to different results (i.e. the results are not directly transferable to different contexts). Variations in feed composition and feed throughput over the operational life of a mine could also give rises to significant differences in environmental performance. As an example, sensitivity analysis has indicated that variability of key parameters (electricity, ore mineralogy and mobilisation of metals), can greatly affect the environmental performance of the two scenarios. The same applies to the fact that electricity grid mix is not the same in most mining sites in the world. For example energy used in South African mines is mostly based on fossil fuel while other countries use renewable energy which might decrease impacts related to electricity production.

(b) Impact categories considered and system boundary

This study focused on seven key impact categories: human toxicity, ecotoxicity, climate change, fossil fuel depletion, terrestrial acidification, urban land occupation and natural land transformation. However, as indicated in Figure 4B, the parameters analysed indicate that the desulphurisation flotation treatment option is also likely to have a significant benefit in terms of recovery of natural resources such as water and minerals. LCIA modelling of water depletion and mineral resource depletion impacts was, however, not conducted in this study, as the relevant upstream and downstream operations for the further processing of these resources did not fall within the defined system boundary. Inclusion of these background processes would have increased input data and information requirements considerably, and was considered beyond the scope of this particular study. It is, furthermore, postulated that the downstream utilisation of desulphurised tailings material, as proposed by Harrison et al. (2013), could also have a significant impact on land use or natural land transformation impacts. Once again, the boundary of the system and the LCI would need to be expanded to include the downstream tailings management processes in order to holistically evaluate their environmental implications.

(c) LCIA modelling capabilities

The results of this study have shown that current commercially-available LCIA models continue to be deficient in terms of the ability to assess many of the impacts of key relevance to solid mineral wastes, particularly aqueous acidification and salinisation of local water resources. As highlighted previously in the literature reviewed these impacts can lead to human and ecotoxic effects and also have adverse effect on the quality of water and usability of water sources, i.e. agricultural uses. There are also uncertainties around modelling of metal impacts. The LCIA results have shown that the metals (especially zinc) make a significant

contribution to human and ecotoxicity impacts and that the relative characterisation factors of the metals assessed are different for the two LCIA methods used. Characterisation factors of metals in LCIA models do not take into account relevant information i.e. metals chemistry, persistence in the environment, speciation and bioavailability. It should also be noted that LCA does not take into account the temporal behaviour of emissions from solid wastes and hence cannot be used to predict actual quality of seepage and water resources in the vicinity of a waste dump.

Chapter 6

CONCLUSIONS AND RECOMMENDATIONS

Xanthate salts, produced by Senmin® International (Pty, Ltd) through the conversion of carbon disulphide at their facility in Sasolburg, South Africa, are commonly used as collectors in the mineral processing of sulphide ores. They have also been used in the desulphurisation flotation of sulphidic mine tailings, with a view to mitigating acid rock drainage (ARD) risks through the pre-disposal removal of sulphide minerals. Having commissioned a new state-of-the-art plant for the production of carbon disulphide, using methane rather than charcoal as a carbon source, no attempt has been made to quantify the environmental benefits of this new process for the production of xanthate in the Sasolburg plant. Similarly, whilst the technical feasibility of using desulphurisation flotation to reduce the ARD generating potential of mine tailings has been demonstrated in a number of case studies, little attention has been given to the broader environmental implications of this tailings treatment option. This study has applied life cycle assessment tools to identify and compare: (i) the environmental impacts of the current and previous carbon disulphide production processes, as well as the subsequent effects of such on xanthate production; (ii) the environmental benefits and/or impacts of the desulphurisation flotation and conventional base metal tailings treatment and management processes, insofar as xanthate is used as a sulphide collector in the desulphurisation process. These objectives were achieved by answering the following research key questions:

(i) How does the environmental performance of the new facility for CS_2 production compare with that of the previous process?

(ii) What effect has the new CS_2 production process had on the environmental performance of subsequent xanthate production?

(iii) How does the environmental performance of the desulphurisation flotation process for the pre-disposal treatment of sulphide tailings compare with the conventional management approach?

(iv) What are the key environmental issues and challenges associated with the proposed desulphurisation flotation process for the mitigation of ARD?

(v) What are the strengths and limitations of current LCA tools in terms of reliably quantifying the systems under investigation in this study?

These research key questions were first addressed through literature review, followed by the application of LCA tools that used a cradle-to-gate and a gate-to-gate system approach.

The first objective of the study was in line with the first two key questions, and was used to address LCA1 (life cycle assessment of xanthate production). To address the second objective, LCA 2 (life cycle assessment of xanthate utilisation in ARD mitigation) was conducted. This was in line with the third and fourth key question of the dissertation, where a case study was applied which involved the treatment of tailings slurry stream generated during the milling and flotation of base metal sulphide ores using xanthate. The results of this study were also used to assess the strengths and limitations of current LCA tools, which were in line with last key question. The outcomes of this study in the light of the key questions stated above are communicated in sections 6.1 and 6.2, while section 6.3 makes recommendations for future work.

6.1 Summary of key research findings

Subsection 6.1.1 summarises the key findings of the LCA 1 (life cycle assessment of xanthate production) study in terms of comparing the environmental impacts of the old and new processes of carbon disulphide and ultimately the effects that these processes have to the subsequent production of xanthate. Subsection 6.1.2 presents key findings of the LCA 2 (life cycle assessment of xanthate utilisation in ARD mitigation) study in light of comparing the environmental impacts of the desulphurisation flotation with the conventional management approach, issues and challenges of the pre-disposal treatment of sulphide tailings and limitations of current LCA tools under the case study.

6.1.1 life cycle assessment of xanthate production (LCA 1)

The foreground inventory analysis of the two compared CS_2 production processes indicate that the new process uses significantly lower energy and water usage, and produce less solid waste by 25%, 67% and 87% respectively. This in turn results in significantly lower environmental impacts, particularly in terms of climate change, human toxicity and freshwater ecotoxicity by 54%, 49%, and 58% respectively, in comparison to the old process.

The consumption of steam, which is produced from coal, contributes significantly to the environmental footprint of CS_2 for both processes. This can be reduced significantly in the new CS_2 process by improving the recovery and reuse of generated steam, especially with respect to climate change, human toxicity and freshwater ecotoxicity (up to a 75%, 93% and 90% improvement respectively, as compared to the old CS_2 process). The xanthate process has a reduced environmental footprint when produced via the new CS_2 process, particularly

in terms of climate change, human toxicity and fresh water ecotoxicity by 39%, 23% and 32% respectively, compared to that produced by the old CS_2 process. Because of its significant contribution to the production of xanthate, the new CS_2 process is a major contributor to the environmental footprint of xanthate, particularly in terms of terrestrial acidification (91% of total) and this can be attributed to SO_2 emissions. Also making a significant contribution to xanthate's life cycle is the production of caustic that contributes a large portion of total human toxicity (60%) and fresh water ecotoxicity (51%), while the production of alcohol makes a substantial contribution to fossil depletion (36%) and climate change (21%).

6.1.2 Life cycle assessment of xanthate utilisation in ARD mitigation (LCA 2)

A comparison of the life cycle inventory data for the two tailings treatment processes indicate that the desulphurisation flotation process consumes more carbon than the conventional process, and results in higher emissions, for instance the emissions for carbon dioxide, sulphur dioxide and xanthate were higher by 76%, 78% and 50% respectively. This is attributed to the additional energy and xanthate required for this process. However, it results in a considerable decrease in the aqueous emissions of acid (99% less), sulphur, as sulphate (89% less) and metals [copper (60% less); zinc (90% less); iron (90% less)], whilst simultaneously enhancing the potential to recover valuable resources, including water and metal values (Cu, Zn and Fe) from the tailings.

LCIA modelling indicated that the incorporation of a desulphurisation flotation unit for the pre-disposal removal of sulphide minerals from tailings results in a significant decrease in both the human and ecotoxicity (89% less) impacts, due predominantly to reduced zinc emissions during subsequent disposal, as well as urban land occupation (27% less) and natural land transformation impacts (26% less). However, desulphurisation flotation also results in an increase in climate change (76% more), fossil fuel depletion (77% more) and terrestrial acidification (77% more) impacts, which can be attributed largely to fossil fuel based electricity production.

Sensitivity analysis results have shown that by varying key parameters (electricity, ore mineralogy and mobilisation of metals), can greatly affect the environmental performance of the two scenarios. In the case of the desulphurisation flotation scenario significant environmental improvements were observed with a decrease in: (1) electricity consumption (40% less), resulting in 39% in climate change, 37 % in both terrestrial acidification and fossil fuel depletion impacts; (2) zinc feed concentration in tailings (90% less), resulting in a 91% and 82% decrease in human toxicity and ecotoxicity impacts respectively; (3) zinc

mobilisation (50% less), resulting in a 52% and 47% decrease in human toxicity and ecotoxicity impacts respectively.

Despite the holistic and systemic nature of the LCA approach, this study has indicated that the existing LCA modelling tools are still deficient in terms of their ability to reliably and comprehensively assess the environmental impacts associated with solid mineral wastes. This pertains, in particular, to aqueous acidification, salinisation and trace metal impacts. There was also poor or no agreement between the two methods (ReCiPe and USEtox) used to analyse toxicity impacts for the compared scenarios, especially with regards to metals, which are characterised by high uncertainty factors. The characterisation factors of metals in USEtox method are marked 'interim', which means they may be used, but with great caution due to their large uncertainty.

6.2 Concluding remarks

The study has successfully demonstrated the application of LCA in the quantitative assessment of the improved environmental performance of the new CS_2 production process relative to the old process, particularly with respect to human and ecotoxicity and climate change. Moreover this has positive environmental impacts on the subsequent performance of the xanthate production process.

LCA has also been used to conduct a holistic assessment of the relative environmental benefits and burdens of using xanthate for the pre-disposal removal of sulphur from tailings, by means of flotation, which results in a significant decrease in human toxicity, ecotoxicity, urban land occupation and natural land transformation impacts, but an increase in climate change, fossil fuel depletion and terrestrial acidification impacts. However, these increases could potentially be offset by avoiding mining emissions if the recovery of metals from the concentrate were included.

Despite limitations with respect to current LCA modelling tools and input data, this study provides useful information in the identification of opportunities for improving environmental performance across the carbon disulphide-xanthate-desulphurisation flotation process system, thus playing a key role in guiding further developmental studies, which are addressed in the next section.

6.3 Recommendations for further work

This section makes recommendations for further work on the desulphurisation flotation process (sub-section 6.3.1) and on the LCIA methodology (subsection 6.3.2)

6.3.1 Recommendations for further development into the desulphurisation flotation process

Further developmental studies are recommended for the desulphurisation flotation process. Firstly, that an experimental analysis is performed for the deportment and behaviour of xanthate salts during desulphurisation flotation and tailings disposal, in order to holistically evaluate their environmental implications to the environment. Secondly, there is a need to obtain and improve the quality of input data and information pertaining to electricity consumption and mobility of tailings components during disposal as this information had a high level of uncertainty in the study.

Thirdly, although not specifically modelled in this study, an analysis of inputs and outputs indicated that the desulphurisation flotation process also has the potential to result in a significant increase in the recovery of valuable resources, including metal values, sulphur and, to a lesser extent, water. To analyse the environmental performance assessment of these recovered resources, it is recommended that an extension of the system boundary and the generation of a life cycle inventory of relevant downstream and upstream processes be incorporated.

6.3.2 Recommendations for further LCIA methodology development

Development of suitable indicators and characterisation factors based within the LCIA methodologies is recommended to adequately assess the environmental performance of the extended desulphurisation flotation process associated with resource depletion and efficient use of the recovered resources.

It is highly recommended that further studies are conducted to develop life cycle indicators and methods which extend and compliment current LCIA methods such as USEtox and ReCiPe, to fully address LCA deficiencies in terms of its ability to assess key relevant emissions related to ARD impacts, particularly aqueous acidification, salinisation and soluble trace metals. This involves improving and developing characterisation factors for these emissions.

It is also recommended that a water assessment study be conducted according to the recently published ISO 14064 standards across the carbon disulphide-xanthate-desulphurisation flotation process system, as the methods for water use (at both inventory and impact assessment levels) in LCA were still undergoing improvement when the study started.

REFERENCES

Agency for Toxic Substances and Disease Registry (ATSDR) 1996. *Toxicological Profile for Carbon disulfide (Update).* (Public Health Service). Atlanta: U.S. Department of Health and Human Services.

Azapagic, A. & Clift, R. 1999. The application of life cycle assessment to process optimisation. *Computers & Chemical Engineering.* 23(10): 1509-1526.

Azapagic, A. 1999. Life cycle assessment and its application to process selection, design and optimisation. *Chemical Engineering Journal.* 73(1): 1-21.

Bauman, H. & Tillman, A. 2004. *The hitch hiker's guide to LCA: an orientation in life cycle assessment methodology and application.* Studentlitteratur.

Benzaazoua, M., Bussière, B., Dagenais, A. & Archambault, M. 2004. Kinetic tests comparison and interpretation for prediction of the Joutel tailings acid generation potential. *Environmental Geology.* 46(8): 1086-1101.

Benzaazoua, M., Bussière, B., Kongolo, M., McLaughlin, J. & Marion, P. 2000. Environmental desulphurisation of four Canadian mine tailings using froth flotation. *International Journal of Mineral Processing.* 60(1): 57-74.

Benzaazoua, M. & Kongolo, M. 2003. Physico-chemical properties of tailing slurries during environmental desulphurisation by froth flotation. *International Journal of Mineral Processing.* 69(1): 221-234.

Bleiwas, D.I. 2012. *Estimated water requirements for the conventional flotation of copper ores.* (2012–1089, 13 p). U.S. Geological Survey Open-File Report.

Block, M. & Pärt, P. 1986. Increased availability of cadmium to perfused rainbow trout (Salmo gairdneri, Rich.) gills in the presence of the complexing agents diethyl dithiocarbamate, ethyl xanthate and isopropyl xanthate. *Aquatic Toxicology.* 8(4): 295-302. DOI:http://dx.doi.org/10.1016/0166-445X(86)90081-0.

Blowes, D.W., Ptacek, C.J., Jambor, J.L. & Weisener, C.G. 2005. The Geochemistry of Acid Mine Drainage. In *Environmental Geochemistry, Treatise on Geochemistry.* Holland, H.D. and Turekian, K.K., Ed. Vol 9 ed. Elsevier-Pergamon, Oxford. 149-204.

Boening, D. 1998. Aquatic toxicity and environmental fate of xanthates. *Mining Engineering.* 50(9): 65-68.

Bois, D., Poirier, P., Benzaazoua, M., Bussière, B. & Kongolo, M. 2005. A feasibility study on the use of desulphurised tailings to control acid mine drainage. *Cim Bulletin.* 98(1087): 1.

Borg, K., Gottofrey, J. & Tjälve, H. 1988. Effects of some chelating agents on the uptake and distribution of 203Hg2 in the brown trout (Salmo trutta): studies on ethyland isopropylxanthate, diethyl-and diisopropyldithiophosphate, dimethyl-and diethyldithiocarbamate and pyridinethione. *Archives of Toxicology.* 62(5): 387-391.

Bradshaw, D. & O'Connor, C. 1994. The flotation of pyrite using mixtures of dithiocarbamates and other thiol collectors. *Minerals Engineering.* 7(5): 681-690.

Broadhurst J., Bryan C., Becker M., Franzidis J-P and Harrison S.T.L. 2013. Characterising the acid generating potential of mine wastes by means of laboratory-scale static and biokinetic tests. In: Brown, A., Figueroa, L. & Wolkersdorfer (eds). *Reliable Mine Water Technology (VoI I): 275-281, Denver, Colorado, USA (ISBN 978-0-615-79385-6).*

Broadhurst, J.L. 2007a. Generalised strategy for predicting environmental characteristics of solid mineral wastes – a focus on copper. *PhD Thesis,University of Cape Town.*

Broadhurst, J., Hansen, Y. & Petrie, J. 2007b. *Waste characterisation and water-related impact predictions for solid mineral wastes: a new approach.* Report No. 1550/1/07 ed. Water Research Commission of South Africa.

Broadhurst, J. & Petrie, J. 2010. Ranking and scoring potential environmental risks from solid mineral wastes. *Minerals Engineering.* 23(3): 182-191.

Broadhurst, J., Petrie, J. & Von Blottnitz, H. 2007c. Understanding element distribution during primary metal production. *Mineral Processing and Extractive Metallurgy.* 116(1): 1-16.

Burgess, A. & Brennan, D. 2001. Application of life cycle assessment to chemical processes. *Chemical Engineering Science.* 56(8): 2589-2604.

Cabral, A., Racine, I., Burnotte, F. & Lefebvre, G. 2000. Diffusion of oxygen through a pulp and paper residue barrier. *Canadian Geotechnical Journal.* 37(1): 201-217.

Chang, Y., Chang, J., Lin, T. & Hsu, Y. 2002. Integrated copper-containing wastewater treatment using xanthate process. *Journal of Hazardous Materials.* 94(1): 89-99. DOI:http://dx.doi.org/10.1016/S0304-3894(02)00060-2.

Chevalier, J., Rousseaux, P., Benoit, V. & Benadda, B. 2003. Environmental assessment of flue gas cleaning processes of municipal solid waste incinerators by means of the life cycle assessment approach. *Chemical Engineering Science.* 58(10): 2053-2064.

Cilliers, J.J. 2006. Active and passive gangue in mineral processing, disposal and economics. *Proceedings of the XXIII International Minerals Processing Congress.* 3-8 September. Istanbul, Turkey.

Clift, R., Frischknecht, R., Huppes, G., Tillman, A. & Weidema, B. 1998. Towards a coherent approach to life cycle inventory analysis. *Unpublished Manuscript.*

Cox, R. & Sheppard, D. 1980. Reactions of OH radicals with gaseous sulphur compounds. *Nature Publishing Group.*

Crozier, R.D. 1992. Flotation. Theory, Reagents and Ore Testing. *Pergamon Press Plc(UK), 1992,*. 356.

Dick, J.,Von Blottnitz, H & Notten, P.J. 2012. South African electricity inventory-Collaboration between The University of Cape Town and The Green House. *Unpublished Manuscript.*

Donoghue, A.M. 1998. Carbon disulphide absorption during xanthate reagent mixing in a gold mine concentrator. *Occupational Medicine (Oxford, England).* 48(7): 469-470.

Donoso, M., Robles, P.A., Gálvez, E.D. & Cisternas, L.A. 2013. Particle size effect on the Efficient Use of Water and Energy in Mineral Concentration Processes. *Industrial & Engineering Chemistry Research.* 52(49): 17686-17690.

Durucan, S., Korre, A. & Munoz-Melendez, G. 2006. Mining life cycle modelling: a cradle-to-gate approach to environmental management in the minerals industry. *Journal of Cleaner Production.* 14(12–13): 1057-1070. DOI:http://dx.doi.org/10.1016/j.jclepro.2004.12.021.

Environmental Protection Agency (EPA) 1986. *Health and Environmental Effects Profile for Carbon Disulfide.* (EPA/600/X-86/155). Cincinnati, Ohio: Environmental Criteria and Assessment Office, U.S.

Farwell, S., Sherrard, A., Pack, M. & Adams, D. 1979. Sulphur compounds volatilised from soils at different moisture contents. *Soil Biology and Biochemistry.* 11(4): 411-415.

Feng, S.C., Joung, C. & Li, G. 2010. Development overview of sustainable manufacturing metrics. *Proceedings of the 17th CIRP International Conference on Life Cycle Engineering.* 6.

Finnveden, G., Hauschild, M.Z., Ekvall, T., Guinée, J., Heijungs, R., Hellweg, S., Koehler, A., Pennington, D. et al. 2009. Recent developments in Life Cycle Assessment. *Journal of Environmental Management.* 91(1): 1-21. DOI:10.1016/j.jenvman.2009.06.018.

Furuholt, E. 1995. Life cycle assessment of gasoline and diesel. *Resources, Conservation and Recycling.* 14(3): 251-263.

Geisler, G., Hofstetter, T.B. & Hungerbühler, K. 2004. Production of fine and speciality chemicals: procedure for the estimation of LCIs. *The International Journal of Life Cycle Assessment.* 9(2): 101-113.

Goedkoop, M., Heijungs, R., Huijbregts, M., De Schryver, A., Struijs, J. & van Zelm, R. 2009. ReCiPe 2008. *A Life Cycle Impact Assessment Method which Comprises Harmonised Category Indicators at the Midpoint and the Endpoint Level.* 1.

Gottofrey, J., Björklund, I. & Tjälve, H. 1988. Effect of sodium isopropylxanthate, potassium amylxanthate and sodium diethyldithiocarbamate on the uptake and distribution of cadmium in the brown trout (Salmo trutta). *Aquatic Toxicology.* 12(2): 171-184. DOI:http://dx.doi.org/10.1016/0166-445X(88)90034-3.

Gray, N. 1997. Environmental impact and remediation of acid mine drainage: a management problem. *Environmental Geology.* 30(1-2): 62-71.

Guinée, J., Gorrée, M., Heijungs, R., Huppes, G., Kleijn, R., De Koning, A., Van Oers, L., Wegener Sleeswijk, A. et al. 2001. Life cycle assessment; An operational guide to the ISO standards; Parts 1 and 2. *Ministry of Housing, Spatial Planning and Environment (VROM) and Centre of Environmental Science (CML), Den Haag and Leiden, the Netherlands.*

Hansen, Y. 2004. Environmental impact assessment of solid waste management in the primary industries–a new approach. *PhD Thesis Dissertation, University of Sydney, Australia.*

Hansen, Y., Broadhurst, J. & Petrie, J. 2008. Modelling leachate generation and mobility from copper sulphide tailings–An integrated approach to impact assessment. *Minerals Engineering.* 21(4): 288-301.

Harris, G.H. 2000. Xanthates. In *Kirk-Othmer Encyclopedia of Chemical Technology.* John Wiley & Sons, Inc.

Harrison S.T.L., Broadhurst, J.L., van Hille, R.P et al. 2010. *Systematic approach to sulphidic waste rock and tailings management to minimise acid rock drainage formation.* (South African Water Research Commission Report No. 1831/1/10). Pretoria, South Africa: WRC.

Hauschild, M.Z. 2005. Assessing environmental impacts in a life-cycle perspective. *Environmental Science & Technology.* 39(4): 81A-88A.

Hauschild, M.Z. & Alting, L. 1998. *Environmental assessment of products: Volume 2: Scientific background.* Springer.

Hauschild, M.Z., Huijbregts, M., Jolliet, O., Macleod, M., Margni, M., van de Meent, D., Rosenbaum, R.K. & McKone, T.E. 2008. Building a model based on scientific consensus for life cycle impact assessment of chemicals: the search for harmony and parsimony. *Environmental Science & Technology.* 42(19): 7032-7037.

Hawley, J.R. 1977. *The use, characteristics and toxicity of mine-mill reagents in the province of Ontario.* Ontario, Canada: Waste Systems Planning Section, Waste Management Branch, Ministry of the Environment.

Heijungs, R., De Koning, A., Ligthart, T. & Korenromp, R. 2004. Improvement of LCA characterisation factors and LCA practice for metals. *TNO Report.* 2004347.

Hesketh, A.H. 2010a. An integrated approach to AMD mitigation through sulphide removal from tailings. *MSc Thesis, University of Cape Town, South Africa.*

Hesketh, A., Broadhurst, J., Bryan, C., van Hille, R. & Harrison, S. 2010b. Biokinetic test for the characterisation of AMD generation potential of sulfide mineral wastes. *Hydrometallurgy.* 104(3): 459-464.

Hesketh, A., Broadhurst, J. & Harrison, S. 2010c. Mitigating the generation of acid mine drainage from copper sulfide tailings impoundments in perpetuity: A case study for an integrated management strategy. *Minerals Engineering.* 23(3): 225-229.

Hischier, R., Weidema, B., Althaus, H., Bauer, C., Doka, G., Dones, R., Frischnecht, R., Jungbluth, N. et al. 2009. ecoinvent database V 2.2.

Hodgkinson, G., Sandenberght, R., Hunter, C. & De Wet, J. 1994. Pyrite flotation from gold leach residues. *Minerals Engineering.* 7(5): 691-698.

IHS Chemicals 2011. *Carbon disulphide.* Available: http://www.ihs.com/products/chemical/planning/ceh/carbon-disulfide.aspx [Accessed March 2013].

International Standards Organisation (ISO) 14040 2006. *Environmental management – Life cycle assessment – Principles and framework.* ISO 14040:2006. European Committee for Standardisation.

Itsubo, N. & Inaba, A. 2003. A new LCIA method: LIME has been completed. *The International Journal of Life Cycle Assessment.* 8(5): 305-305.

Jefferies, D., Muñoz, I., Hodges, J., King, V.J., Aldaya, M., Ercin, A.E., i Canals, L.M. & Hoekstra, A.Y. 2012. Water footprint and life cycle assessment as approaches to assess potential impacts of products on water consumption. Key learning points from pilot studies on tea and margarine. *Journal of Cleaner Production.* 33155-166.

Jennings, S.R., Blicker, P.S., Neuman, D.R. & Reclamation Research Group. 2008. *Acid mine drainage and effects on fish health and ecology: a review.* Reclamation Research Group.

Jiménez-González, C., Curzons, A.D., Constable, D.J. & Cunningham, V.L. 2004. Cradle-to-gate life cycle inventory and assessment of pharmaceutical compounds. *The International Journal of Life Cycle Assessment.* 9(2): 114-121.

Jiménez-González, C., Kim, S. & Overcash, M.R. 2000. Methodology for developing gate-to-gate life cycle inventory information. *The International Journal of Life Cycle Assessment.* 5(3): 153-159.

Jolliet, O., Brent, A., Goedkoop, M., Itsubo, N., Mueller-Wenk, R., Peña, C., Schenk, R., Stewart, M. et al. 2003. Final report of the LCIA Definition study. *Life Cycle Impact Assessment Programme of the Life Cycle Initiative.*

Jolliet, O., Margni, M., Charles, R., Humbert, S., Payet, J., Rebitzer, G. & Rosenbaum, R. 2003. IMPACT 2002 : a new life cycle impact assessment methodology. *The International Journal of Life Cycle Assessment.* 8(6): 324-330.

Kazadi Mbamba, C. 2011. Using froth flotation to mitigate acid rock drainage risks while recovering valuable coal from ultrafine wastes. *MSc Thesis, University of Cape Town, South Africa.*

Kazadi Mbamba, C., Harrison, S.T.L., Franzidis, J.-. & Broadhurst, J.L. 2012. Mitigating acid rock drainage risks while recovering low-sulphur coal from ultrafine colliery wastes using froth flotation. *Minerals Engineering.* 29(0): 13-21. DOI:10.1016/j.mineng.2012.02.001.

Keller, C.H. 1927. Froth-flotation concentration of ores. *United States Patent Number.* 1 671 590.

Kim, S. & Overcash, M. 2003. Energy in chemical manufacturing processes: gate-to-gate information for life cycle assessment. *Journal of Chemical Technology and Biotechnology.* 78(9): 995-1005.

Klinglmair, M., Sala, S. & Brandão, M. 2014. Assessing resource depletion in LCA: a review of methods and methodological issues. *The International Journal of Life Cycle Assessment.* 19(3): 580-592.

Klöpffer, W. 2005. Life Cycle Assessment as Part of Sustainability Assessment for Chemicals (5 pp). *Environmental Science and Pollution Research.* 12(3): 173-177.

Koroneos, C., Dompros, A., Roumbas, G. & Moussiopoulos, N. 2004. Life cycle assessment of hydrogen fuel production processes. *International Journal of Hydrogen Energy.* 29(14): 1443-1450.

Lay, M.D.S., Sauerhoff, M.W. & Saunders, D.R. 2000. Carbon Disulfide. In *Ullmann's Encyclopedia of Industrial Chemistry.* Wiley-VCH Verlag GmbH & Co. KGaA.

Lesage, P., Reid, C., Margni, M., Aubertin, M. & Deschênes, L. 2008. Use of LCA in the mining industry and research challenges. *CIRAIG, École Polytechnique De Montréal, Québec.Industrial NSERC Polytechnique-UQAT Chair, Environmental and Mine Wastes Management, École Polytechnique De Montréal, Québec.*

Lottermoser, B. 2010. *Mine wastes: characterisation, treatment and environmental impacts.* Springer.

Mangena, S.J. & Brent, A.C. 2006. Application of a Life Cycle Impact Assessment framework to evaluate and compare environmental performances with economic values of supplied coal products. *Journal of Cleaner Production.* 14(12–13): 1071-1084. DOI:http://dx.doi.org/10.1016/j.jclepro.2004.04.012.

Marsden, J.O. 2008. Energy efficiency and copper hydrometallurgy. *Proc. Hydrometallurgy 2008 Symposium in Honor of Robert S. Shoemaker, Phoenix, Arisona. Society for Mining, Metallurgy & Exploration, Inc., Littleton, Colorado.* 29.

Milà i Canals, L., Chenoweth, J., Chapagain, A., Orr, S., Antón, A., Clift, R. 2009. Assessing freshwater use impacts in LCA: Part I - inventory modeling and characterization factors for the main impact pathways. *The International Journal of Life Cycle Assessment.* 14 (1): 28-42

Moore, C. 1994. Canadian Centre for Occupational Health and Safety (CCOHS). *Liaison, A Newsletter for the Users ofCCINFO.* 9(4): 4.

Mwale, A., Musonge, P. & Fraser, D. 2005. The influence of particle size on energy consumption and water recovery in comminution and dewatering systems. *Minerals Engineering.* 18(9): 915-926.

Napier-Munn, T., Parbhaker, A., Edraki, M. and Bradshaw, D.J. 2008. Managing ARD Potential through Mine Planning and Mineral Processing Practice. *Sixth Australian Workshop on Acid and Metalliferous Drainage.* 15-18 April. Burnie, Tasmania.

National Industrial Chemicals Notification and Assessment Scheme (NICNAS) 1995. *Sodium Ethyl Xanthate.* (Full Public Report, Priority Existing Chemical No. 5). Canberra: AGPS.

National Industrial Chemicals Notification and Assessment Scheme (NICNAS) 2000. *Sodium Ethyl Xanthate.* (Priority Existing Chemical Secondary Notification Assessment Report No.5S).

National Environmental Management (NEM): Air Quality Act (39/2004). 2010. *List of atmospheric emissions which have or may have a significant detrimental effect on the environment, including health, social, economic, ecological conditions or cultural heritage*. Pretoria, South Africa.

National Occupational Health and Safety Commission (NOHSC). 1999. *List of Designated Hazardous Substance.* second edition ed. Canberra: AGPS.

Newhook, R., Meek, M. & Caldbick, D. 2002. Concise International Chemical Assessment Document (CICAD) 46: Carbon disulfide. *World Health Organisation (WHO): Geneva.*

Norgate, T. & Haque, N. 2010. Energy and greenhouse gas impacts of mining and mineral processing operations. *Journal of Cleaner Production.* 18(3): 266-274.

Norgate, T. 2001. A Comparative Life Cycle Assessment of Copper Production Processes. *Clayton South: CSIRO Minerals.*

Norgate, T., Jahanshahi, S. & Rankin, W. 2007. Assessing the environmental impact of metal production processes. *Journal of Cleaner Production.* 15(8): 838-848.

Norgate, T. & Rankin, W. 2000. Life cycle assessment of copper and nickel production. *Proceedings of MINPREX.* 2000133-138.

Notten, P.J. 2001. Life cycle inventory uncertainty in resource-based industries – A focus on coal-based power generation. *PhD Thesis Dissertation, University of Cape Town, South Africa.*

Occupational Safety and Health Administration (OSHA) 1995. *Air Contaminants.* (Code of Federal Regulations 29 CFR 1910.20). U.S. Department of Labor.

O'Connor, C. & Dunne, R. 1991. The practice of pyrite flotation in South Africa and Australia. *Minerals Engineering.* 4(7): 1057-1069.

Peyton, T.O., Steele, R.V. & Mabey, W.R. 1978. *Carbon disulfide, carbonyl sulfide: Literature review and environmental assessment.* Environmental Protection Agency, Office of Health and Ecological Effects.

Pizzol, M., Christensen, P., Schmidt, J. & Thomsen, M. 2011a. Ecotoxicological impact of "metals" on the aquatic and terrestrial ecosystem: a comparison between eight different methodologies for life cycle impact assessment (LCIA). *Journal of Cleaner Production.* 19(6): 687-698.

Pizzol, M., Christensen, P., Schmidt, J. & Thomsen, M. 2011b. Impacts of "metals" on human health: a comparison between nine different methodologies for Life Cycle Impact Assessment (LCIA). *Journal of Cleaner Production.* 19(6): 646-656.

Portha, J., Jaubert, J., Louret, S. & Pons, M. 2010. Life cycle assessment applied to naphtha catalytic reforming. *Oil & Gas Science and Technology–Revue d'IFP Energies Nouvelles.* 65(5): 793-805.

PRé Consultants 2012. SimaPro 7, Life-cycle Assessment Software Package, Version 7.3.3. *Printerweg, Amersfoort, the Netherlands.*

Qun Yan, Jun-wen Huang, Mei-xiang Tang & Yang Yu 2011. Experimental study on the treatment of butyl xanthate from beneficiation wastewater by sodium hypochlorite. *Electric Technology and Civil Engineering (ICETCE), 2011 International Conference on.* 1262.

Read, A. & Manser, R. 1975. Residual flotation reagents: Problems in effluent disposal and water recycle. *Proceedings XI Mineral Processing Congress.* 1323.

Reid, C., Aubertin, M., Deschênes, L., Bussière, B. & Bécaert, V. 2007. Application of life cycle assessment (LCA) to sulphidic tailings management. *Mining and the Environment IV Conference.* 19.

Reid, C., Bécaert, V., Aubertin, M., Rosenbaum, R.K. & Deschênes, L. 2009. Life cycle assessment of mine tailings management in Canada. *Journal of Cleaner Production.* 17(4): 471-479.

Ricard, J., Aubertin, M., Firlotte, F., Knapp, R., McMullen, J. & Julien, M. 1997. Design and construction of a dry cover made of tailings for the closure of Les Terrains Aurifères site, Malartic, Québec, Canada. *Proceedings of the 4th International Conference on Acid Rock Drainage, Vancouver, BC.* 1515.

Ripley, E.A. & Redmann, R.E. 1995. *Environmental effects of mining.* CRC Press.

Rosenbaum, R.K., Bachmann, T.M., Gold, L.S., Huijbregts, M.A., Jolliet, O., Juraske, R., Koehler, A., Larsen, H.F. et al. 2008. USEtox—the UNEP-SETAC toxicity model: recommended characterisation factors for human toxicity and freshwater ecotoxicity in life cycle impact assessment. *The International Journal of Life Cycle Assessment.* 13(7): 532-546.

Rostad, C.E., Schmitt, C.J., Schumacher, J.G. & Leiker, T.J. 2011. An Exploratory Investigation of Polar Organic Compounds in Waters from a Lead–Zinc Mine and Mill Complex. *Water, Air, & Soil Pollution.* 217(1-4): 431-443.

Roy, K. 2000. Xanthates. In *Ullmann's Encyclopedia of Industrial Chemistry.* Wiley-VCH Verlag GmbH & Co. KGaA.

Scientific Applications International Corporation (SAIC) & Curran, M.A. 2006. *Life-cycle Assessment: Principles and Practice.* National Risk Management Research Laboratory, Office of Research and Development, US Environmental Protection Agency.

Simms, P.H., Yanful, E.K., St-Arnaud, L. & Aubé, B. 2000. A laboratory evaluation of metal release and transport in flooded pre-oxidised mine tailings. *Applied Geochemistry.* 15(9): 1245-1263.

Smith, D.E. & Timmerman, R.W. 2000. Carbon Disulfide. In *Kirk-Othmer Encyclopedia of Chemical Technology.* John Wiley & Sons, Inc.

Sobek, A., Schuller, W., Freeman, J. & Smith, R. 1978. *Field and Laboratory Methods Applicable to Overburdens and Minerals.US Environmental Protection Agency.*

Stewart, M. 2001. Report on the MMSD Life Cycle Assessment Workshop: the application of Life Cycle Assessment to mining, minerals and metals. *New York.*

Stewart, M., Hansen, Y. & Petrie, J. 2004. Critical issues for life cycle impact assessment in minerals processing and metals refining. *Green Processing 2004.* 2179-184.

Stewart, M. & Petrie, J. 1999. Planning for waste management and disposal in minerals processing using life cycle assessment. *Minerals and Energy.* 14(4): 14-36.

Stewart, W.A., Miller, S.D. & Smart, R. 2006. Advances in acid rock drainage (ARD) characterisation of mine wastes. *Asmr.*

Suppen, N., Carranza, M., Huerta, M. & Hernández, M.A. 2006. Environmental management and life cycle approaches in the Mexican mining industry. *Journal of Cleaner Production.* 14(12–13): 1101-1115. DOI:http://dx.doi.org/10.1016/j.jclepro.2004.12.020.

Swart, P. & Dewulf, J. 2013. Quantifying the impacts of primary metal resource use in life cycle assessment based on recent mining data. *Resources, Conservation and Recycling.* 73180-187.

Tan, R.B.H. & Khoo, H.H. 2005. An LCA study of a primary aluminum supply chain. *Journal of Cleaner Production.* 13(6): 607-618. DOI:http://dx.doi.org/10.1016/j.jclepro.2003.12.022.

The International Network for Acid Prevention (INAP) 2009. *Global Acid Rock Drainage Guide (GARD Guide).* Available: http://www.gardguide.com/ [Accessed 20-March-2013].

Tillman, A. 2000. Significance of decision-making for LCA methodology. *Environmental Impact Assessment Review.* 20(1): 113-123.

Tillman, A., Svingby, M. & Lundström, H. 1998. Life cycle assessment of municipal waste water systems. *The International Journal of Life Cycle Assessment.* 3(3): 145-157.

Valente, T. & Gomes, C.L. 2007. The role of two acidophilic algae as ecological indicators of acid mine drainage sites. *Journal of Iberian Geology.* 33(2): 283-294.

Van Damme, P.A., Hamel, C., Ayala, A. & Bervoets, L. 2008. Macroinvertebrate community response to acid mine drainage in rivers of the High Andes (Bolivia). *Environmental Pollution.* 156(3): 1061-1068. DOI:http://dx.doi.org/10.1016/j.envpol.2008.04.018.

Vigon, B.W., Tolle, D.A., Evers, D.P., Freeman, S.L., Humphreys, K.K., Wend, C.F. & Landucci, R. 1996. Life cycle assessment of biomass conversion to feedstock chemicals. *Energy Conversion Engineering Conference, 1996. IECEC 96., Proceedings of the 31st Intersociety.* IEEE. 2128.

Von Bahr, B. & Steen, B. 2004. Reducing epistemological uncertainty in life cycle inventory. *Journal of Cleaner Production.* 12(4): 369-388.

Webb, M., Ruber, H. & Leduc, G. 1976. The toxicity of various mining flotation reagents to rainbow trout (Salmo gairdneri). *Water Research.* 10(4): 303-306.

Wernet, G., Conradt, S., Isenring, H.P., Jiménez-González, C. & Hungerbühler, K. 2010. Life cycle assessment of fine chemical production: a case study of pharmaceutical synthesis. *The International Journal of Life Cycle Assessment.* 15(3): 294-303.

Wills, B.A. 2011. *Wills' mineral processing technology: an introduction to the practical aspects of ore treatment and mineral recovery.* Butterworth-Heinemann.

World Health Organisation (WHO) 1979. *Environmental Health Criteria 10: Carbon disulfide.* Geneva, Switzerland: United Nations Environment Programme.

Xu, Y., Lay, J.P., and Korte, F 1988. Fate and effects of xanthates in laboratory freshwater systems. *Bull. Environ. Contam. Toxicol.* 41683-689.

Zeise, W. 1822. Schweiggers. *J.Chem.Phys.* 35(173): 36.

Websites consulted

Life cycle initiative, http://www.lifecycleinitiative.org, consulted in April, 2014

GaBi Software, www.gabi-software.com, consulted in April, 2013.

GEMIS, www.oeko.de/service/gemis/en/, consulted in April, 2013.

BEES, http://www.nist.gov/el/economics/BEESSoftware.cfm, consulted in April, 2013

APPENDICES

List of appendices

APPENDIX A: Attenuation and net availability of selected elements in typical copper sulphide tailings impoundments

Table A1: Attenuation and net availability of selected elements in typical copper sulphide tailings impoundments (Broadhurst, 2007a)

Element	Dominant attenuation mechanism(s)	Attenuation potential factor	Availability potential factor
Extensive attenuation			
Arsenic	Adsorption onto hydrated ferric oxides	0.98-1.00	<0.02
Lead	• Precipitation of anglesite ($PbSO_4$) and/or • Adsorption by ferrihydrite	0.99-1.00	<0.01
Selenium	Precipitation of copper selenides (Cu_2Se).	0.95-1.00	<0.05
Molybdenum	• Precipitation of calcium molybdate ($CaMO_4$) and/or • Adsorption by ferrihydrite	0.98-1.00	<0.02
Antimony	Precipitation of oxides $Sb(OH)_3$ and/or Sb_2O_4	0.97-1.00	<0.03
Iron	Precipitation of jarosite, ferrihydrite, goethite and, to a lesser extent, schwertmannite	0.97-1.00	<0.03
Tellurium	Precipitation of Cu_2Te and/or TeO	0.99-1.00	<0.01
Silver	Formation of metallic Ag	>0.99	<0.01
Bismuth	Precipitation of Bi_2O_3	0.98-1.00	<0.02
Aluminium	Precipitation of alunite, gibbsite and, to lesser extent , jurbanite and kaolinite	0.99-1.00	<0.003
Copper	• Metallic copper formation and, to a lesser extent, chalcocite (Cu_2S) • Adsorption by ferrihydrite	0.9-1.0	<0.1
Mercury	Metallic Hg	>0.99	<0.01
Barium	Precipitation of barite ($BaSO_4$)	>0.99	<0.01
Platinum	Formation of metallic Pt	>0.99	<0.01
Tungsten	• Precipitation of $CaWO_4$ • Adsorption by ferrihydrite	>0.98	<0.02

Element	Dominant attenuation mechanism(s)	Attenuation potential factor	Availability potential factor
Partial attenuation			
Cadmium	• Adsorption by ferrihydrite. • Partial precipitation of $CdCO_3$ possible at pH ≥ 6.	0.35-0.85	0.15-0.60
Zinc	• Adsorption by ferrihydrite • Partial precipitation of $ZnCO_3$ possible at pH ≥ 6.5	0.20-0.50	0.45-0.75
Nickel	Adsorption by ferrihydrite	0.25-0.85	0.15-0.70
Calcium	Precipitation of gypsum ($CaSO_4.2H_2O$)	0-0.40	0.30-0.80
K and Na	Precipitation of jarosites	0-1.00	0-0.30
Low attenuation			
Manganese	• Adsorption by ferrihydrite. • Partial precipitation of $MnCO_3$ possible at pH ≥ 6.	<0.25	0.60-0.95
Sulphur	• Precipitation of gypsum and hydroxy sulphates of Fe and Al • Partial adsorption by ferrihydrite possible	<0.20	>0.70
Germanium	Precipitation of GeO_2	<0.01	>0.90
Boron	Adsorption by ferrihydrite	<0.07	0.10-0.30
Magnesium	Adsorption by ferrihydrite	<0.05	0.45-0.80

APPENDIX B: Old CS_2 process

Table B 1: Input and output raw data for old CS_2 process

Year 2009	Electricity	Steam	Fuel gas	Total energy	Water	Nitrogen	Solid waste	Hazardous waste	Liquid effluent	SO_2
Month	**GJ**	**GJ**	**GJ**	**GJ**	**m^3**	**m^3**	**kg**	**kg**	**m^3**	**kg**
Jan-09	3257.17	7214.158	339.11	10810.44	2392	28400.00	4278.19	4650	336.00	3369
Feb-09	3569.05	6774.236	498.01	10841.29	2401	31725.00	7617.75	7150	350.00	13476
Mar-09	3900.07	7965.496	945.25	12810.82	2688	31162.50	10416.07	10850	365.00	23583
Apr-09	3578.41	7242.298	1063.28	11883.99	3141	32000.00	5080.83	4800	365.03	26952
May-09	2743.77	6582.884	963.01	10289.66	2487	35000.00	3310.65	3900	383.00	10107
Jun-09	3934.95	7744.128	1128.34	12807.42	2541	35075.00	92891.78	8200	406.00	43797
Jul-09	3480.21	6456.254	1153.68	11090.14	2051	32712.50	40259.49	8150	356.00	30321
Aug-09	3347.87	8655.864	868.00	12871.73	2789	28587.50	7002.31	8250	324.00	57273
Sep-09	3421.92	8602.398	687.00	12711.31	3235	31787.50	28575.86	32950	364.00	20214
Oct-09	4177.09	10721.34	798.45	15696.88	3183	29487.50	7793.78	8450	338.00	23583
Nov-09	3397.55	9838.682	5631.28	18867.52	2594	34262.50	4663.00	5350	376.00	0
Dec-09	4090.77	8676.5	677.43	13444.70	2911	25450.00	128364.57	14200	678.00	3369
Total	42898.82	96474.24	14752.84	154125.90	32413	375650.00	340254.26	116900	4641.01	256044
Average	3574.90	8039.52	1229.40	12843.82	2701.08	31304.17	28354.52	9741.67	386.75	21337
Unit per tonne of CS_2	5.66	12.73	1.95	20.34	4.28	49.57	24.61	8.45	0.34	33.78

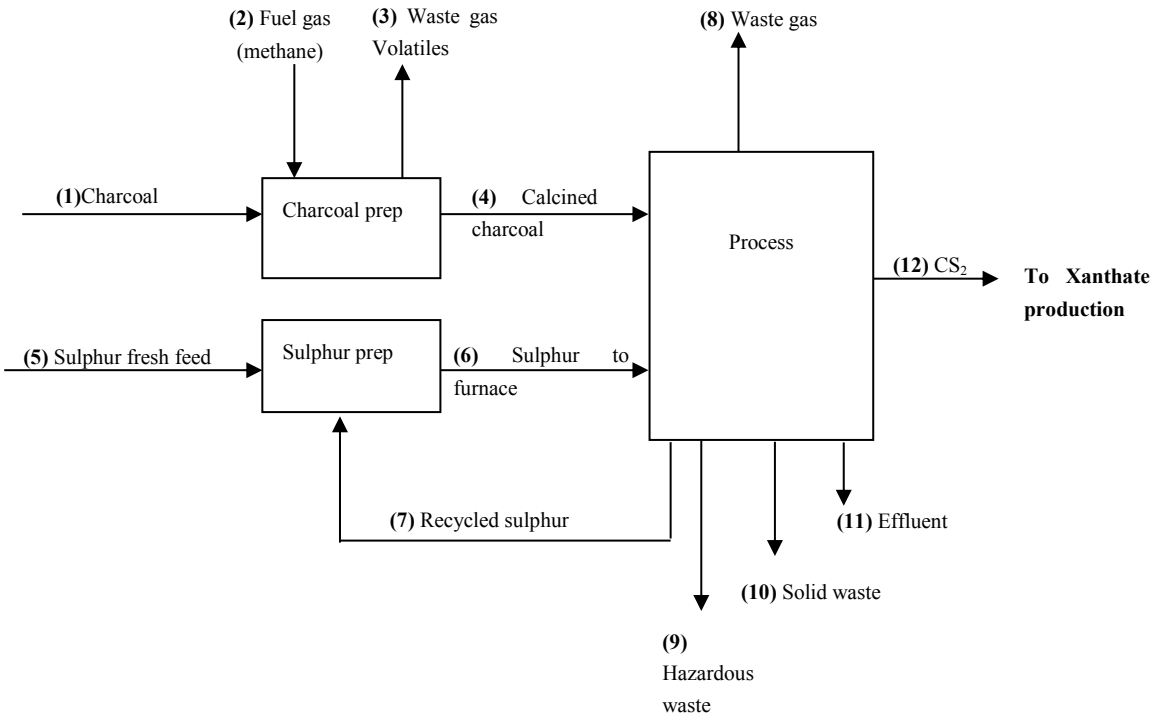


Figure B 1: Simplified Flow sheet of old CS_2 process

Table B 2: Key mass flow parameters per tonne of CS_2 produced (Old CS_2 process)

Unit operation	**Charcoal preparation**				**Sulphur preparation**			**Carbon disulphide production**				
Description	**charcoal**	**fuel gas**	**waste gas**	**calcined charcoal**	**fresh sulphur**	**feed sulphur**	**recycled sulphur**	**waste gas**	**hazardous waste**	**solid waste**	**effluent**	**product gas**
Stream number	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**
Units	**kg**	**kg**	**kg**	**kg**	**kg**	**kg**	**kg**	**kg**	**Kg**	**kg**	**m^3**	**kg**
Carbon species												
Solid carbon	185.58	-	0.00	185.58	-	-	-			16.98		
CO_2	-	-	96.32	-	-	-	-	11.61				
methane (CH_4)	-	35.10	-	-	-	-	-	-				
CS_2	-	-	-	-	-	-	-	-	8.281			1000
Sulphur species												
elemental sulphur	-	-	-	-	891.82	990.91	99.09	-	0.0848			10.20
H_2S	-	-	-	-	-	-	-	-	0.0338			4.08
Sulphur dioxide								33.78				
Other												
entrained moisture	11.18	-	9.16	2.02	0.45	0.50	0.050	2.47				
Water			78.88								0.34	
ash	4.47	-	0.44	4.03	3.59	3.99	0.399	-		7.62		
arsenic	-	-	-	-	0.00	0.00	0.000	-				
bitumen	-	-	-	-	2.69	2.99	0.299	-				
Volatiles	22.36	-	12.27	10.09	-	-	-	10.09				
Total	224	35.10	197.07	201.72	898.56	998.40	99.84	57.95	8.45	24.61	0.34	1020.41

Table B 3: Mass flows in streams (Old CS_2 process)

Stream No	Calculations	Assumptions and information
1	$M_{carbon(1)} = (M_{CS2} * Mw_{carbon}/Mw_{CS2})/85\%$ $M_{charcoal(1)} = M_{carbon(1)} / C_{carbon(1)}$ $M_{moisture(1)} = M_{charcoal(1)} * C_{moisture(1)}$ $M_{ash(1)} = M_{charcoal(1)} * C_{ash(1)}$ $M_{volatiles(1)} = M_{charcoal(1)} * C_{volatiles(1)}$	• The conversion efficiency in the furnace is 85% (based on discussions with plant personnel). • The charcoal calcination process does not result in any loss of solid carbon.
2	$M_{methane(2)} = (G_{fuel\ gas}/H_{methane}) * 10\text{^}6 * Mw_{methane}/1000$ $M_{natural\ gas(2)} = M_{methane(2)} * 0.98$	Methane content in natural gas is 98 mass %
3	$M_{CO2(3)}=(G_{fuel\ gas}/H_{methane}) * 10\text{^}6 * Mw_{CO2}/1000$ $M_{water(3)}=(G_{fuel\ gas}/H_{methane}) * 10\text{^}6 * Mw_{H2O}/1000$ $M_{moisture(3)} = M_{moisture(3)} - M_{moisture(4)}$ $M_{ash(3)} = M_{ash(1)} - M_{ash(4)}$ $M_{volatiles(3)} = M_{volatiles(1)} - M_{volatiles(4)}$	Waste gas contains CO_2 and water generated through the combustion of fuel gas, as well as moisture, ash and volatiles from the feed charcoal.
4	$M_{carbon(4)}=M_{carbon(1)}$ $M_{calcined\ charcoal(4)}=M_{carbon(4)}/C_{carbon(4)}$ $M_{moisture(4)} = M_{calcined\ charcoal(4)} * C_{water(4)}$ $M_{ash(4)} = M_{calcined\ charcoal(4)} * C_{ash(1)}$ $M_{volatiles(4)} = M_{calcined\ charcoal(4)} * C_{volatiles(4)}$	The charcoal calcination process does not result in any loss of solid carbon.
6	$M_{So(6)} = (M_{CS2} * 2*Mw_{sulphur}/Mw_{CS2})/85\%$ $M_{total\ S(6)} = M_{So(6)} / C_{So(6)}$ $M_{moisture(6)} = M_{total\ S(6)} * C_{moisture(6)}$ $M_{ash(6)} = M_{total\ S(6)} * C_{ash(6)}$ $M_{arsenic(6)} = M_{total\ S(6)} * C_{arsenic\ (6)}$ $M_{bitumen(6)} = M_{total\ S(6)} * C_{bitumen\ (6)}$	Extent of conversion of sulphur to carbon disulphide is 85% (based on communications with plant personnel)

7	$M_{total\ S(7)} = M_{total\ S(6)} * 10\%$ $M_{So(7)} = M_{total\ S(7)} * C_{So(7)}$ $M_{moisture(7)} = M_{total\ S(7)} * C_{moisture(7)}$ $M_{ash(7)} = M_{total\ S(7)} * C_{ash(7)}$ $M_{arsenic(7)} = M_{total\ S(7)} * C_{arsenic(7)}$ $M_{bitumen(7)} = M_{total\ S(7)} * C_{bitumen(7)}$	10% of the total feed sulphur to the reactor is recycled (in accordance with design specifications)
8	$M_{CO2(8)} = M_{SO2(8)} * Mw_{CO2}/(Mw_{SO2} * 2)$ $M_{moisture(8)} = (M_{moisture(4)} + M_{moisture(6)}) - M_{moisture(11)}$ $M_{volatiles(8)} = M_{volatiles(4)} - M_{moisture(11)}$	• Stoichiometric CO_2 release assumed • M_{SO2} is taken from the production sheet • All residual moisture and volatiles in the charcoal and sulphur feed streams report to the product and waste gas streams
9	$M_{CS2(9)} = M_{hazardous\ waste(9)} * C_{CS2(11)}$ $M_{So(9)} = M_{hazardous\ waste(9)} * C_{So(11)}$ $M_{H2S(9)} = M_{hazardous\ waste(9)} * C_{H2S(11)}$ $M_{residue(9)} = M_{hazardous\ waste(9)} * C_{residue(11)}$	• The hazardous waste stream comprises largely CS_2 with the same chemical composition as the product stream • Total flow of hazardous waste is taken from the production sheet
10	$M_{carbon(10)} = M_{solid\ waste(10)} - M_{ash(10)}$ $M_{ash(10)} = (M_{ash(4)} + M_{ash(6)}) - M_{ash(11)}$	• The solid waste stream comprises the balance of the ash (product-feed) and solid carbon. • The total sold waste flow is taken from the production sheet
11	$M_{total\ product\ (11)} = M_{CS2(11)} / C_{CS2(11)}$ $M_{So(11)} = M_{total\ product\ (11)} * C_{So(11)}$ $M_{H2S(11)} = M_{total\ product\ (11)} * C_{H2S(11)}$ $M_{residue(11)} = M_{total\ product\ (11)} * C_{residue(11)}$	$M_{CS2(11)} = 1000$ (unit flow)
	Where: $M_{x(y)}$ = unit mass flow per tonne of CS_2 of component x in stream no y Mw_x= molar mass of species x $C_{x(y)}$ = concentration (%) of component x in stream no y (see chemical compositions below) $G_{fuel\ gas}$ = Gas energy (GJ) of fuel gas per tonne of CS_2 in stream 2 = 1.95 GJ (production sheet) $H_{methane}$ = Heat of combustion of methane = 891 kJ/mol Reaction in furnace: $C + 2S = CS_2$ Combustion of fuel gas in calciner: $CH_4 + 2O_2 = CO_2 + 2H_2O$ Busting of safety disc: $CS_2 + 3O_2 = 2SO_2 + CO_2$	

Table B 4: Stream Compositions (Old CS_2 process)

Component (Mass %)	Fresh charcoal	Calcined charcoal	Fresh Sulphur	CS_2 product
	S1	**S4**	**S6**	**S11**
Carbon	83	92	-	-
Ash	2	2	0.4	-
Moisture	5	1	0.05	-
Volatiles	10	5	-	-
Elemental Sulphur	-	-	99.25	1
Bitumen	-	-	0.3	-
Arsenic	-	-	0	-
CS_2	-	-	-	98
H_2S	-	-	-	0.4
Other (residue)	-	-	-	0.6

APPENDIX C: New CS_2 process

Table C 1 : Input and output raw data for new CS_2 process

Year 2011	Electricity	Steam used	Steam produced	Total natural gas	Total energy	Water	Nitrogen	Solid waste	Hazardous waste	Liquid effluent	SO_2	CO_2
Month	**GJ**	**tonne**	**tonne**	**kg**	**GJ**	**m^3**	**m^3**	**Kg**	**kg**	**m^3**	**kg**	**Kg**
Jan	431	4276	-	84147	16796	1410	10208	0	6350	101	0	0
Feb	788	2610	-	375229	15045	1381	0	0	0	613	43829	331240
Mar	891	2506	-	416829	15455	1543	3950	3499	3500	674	50546	362476
Apr	953	2888	1337	414001	16438	1374	6190	0	0	695	50389	357214
May	802	2908	839	316423	14899	1248	6703	0	0	546	37571	284969
Jun	827	3329	992	345025	16711	1225	9558	0	0	558	40657	322845
Jul	849	3461	101	342980	17012	1118	4959	0	0	524	36232	321990
Aug	535	4121	225	247938	22742	1127	4086	13100	13100	101	4677	520026
Sep	878	2707	1502	441745	16541	1378	15253	0	0	710	53090	395023
Oct	915	3014	1524	484585	18081	1636	25102	0	0	783	57108	420998
Nov	903	2757	1565	479465	17176	1525	40202	5399	5400	757	57520	403730
Dec	839	3422	1412	396434	17799	1316	27873	0	0	579	46712	349796
Total	9618	37999	10412	4344801	204700	16286	154088	21999	28350	6641	478331	4279673
Ave.	801	3166.58	1156	362066	17058	1357	12840	1833	2362.5	553.42	39860	356639
Unit per tonne of CS_2	0.81	3.217	0.9	367.8	17.33	1.38	13.05	1.86	2.40	0.56	40.50	362.36

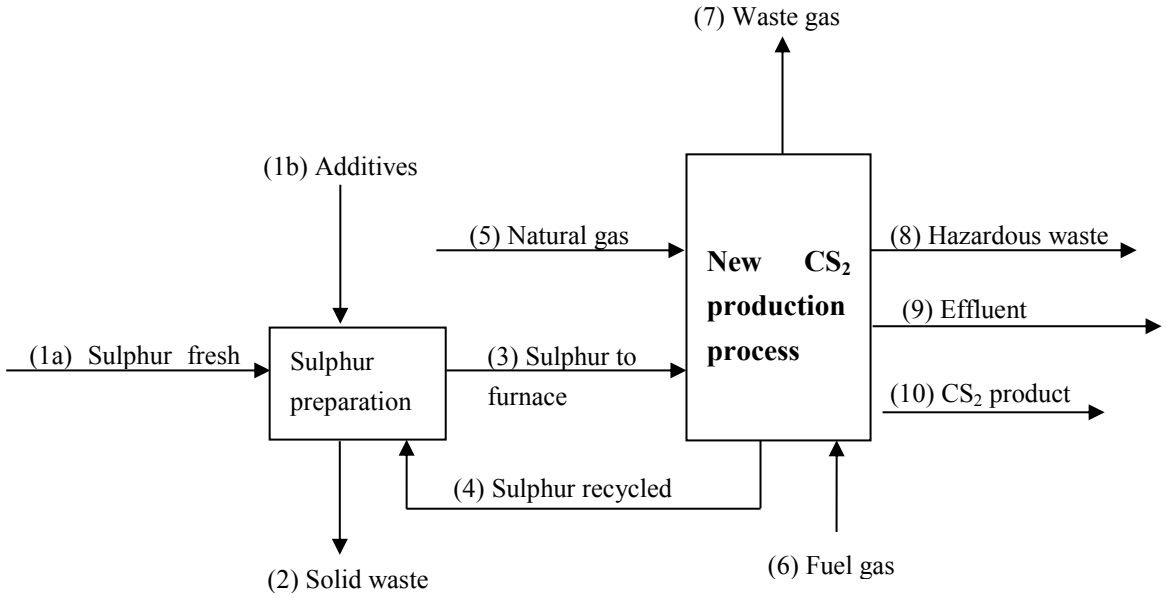


Figure C 1: Simplified Flow sheet for new CS_2 process

Table C 2: Key mass flow parameters per tonne of CS_2 produced (New CS_2 process)

Unit operation			**Sulphur preparation**				**Carbon disulphide production**				
Description	Fresh sulphur	Additives	Solid waste	Feed sulphur	Recycled sulphur	Natural gas	Fuel gas	Waste gas	Hazardous waste	Effluent	Product gas
Stream number	1a	1b	2	3	4	5	6	7	8	9	10
Units	kg	kg	kg	kg	kg	kg	Kg	Kg	kg	m^3	kg
Carbon species											
CO_2								362.36			
Methane (CH_4)						219.54	140.97				
CS_2									2.352		1000.00
Sulphur species											
Elemental sulphur	877.37		1.11	965.11	87.74				0.024		10.20
H_2S									0.0096		4.08
Sulphur dioxide								40.5			
Other											
Ashes	0.89		0.16	0.89	0.89						
Organic substances C	1.33		0.21	1.33	1.33						
Acid	0.18			0.18	0.18						
Entrained moisture	1.77			1.77	1.77						
Water										0.56	
Arsenic	0.27			0.27	0.27						
Lime (CaOH)2		0.17									
Filter aid		0.35	0.05								
Activated clay		2	0.27								
CaSO4			0.05								
Other (residue)									0.0144		6.12
Total	881.78	2.52	1.86	969.96	88.18	219.54	140.97	402.86	2.4	0.56	1020.41

Table C 3: Mass flows in stream (New CS_2 process)

Stream No	Calculations	Assumptions and information
1a	$M_{So(1a)} = (M_{CS2} * 2*Mw_{sulphur}/Mw_{CS2})/96\%$ $M_{total\ S(1a)} = M_{So(1a)} / C_{So(1a)}$ $M_{moisture(1a)} = M_{total\ S(1a)} * C_{moisture(1a)}$ $M_{ash(1a)} = M_{total\ S(1a)} * C_{ash(1a)}$ $M_{arsenic(1a)} = M_{total\ S(1a)} * C_{arsenic\ (1a)}$ $M_{acid(1a)} = M_{total\ S(1a)} * C_{acid\ (1a)}$ $M_{carbon(1a)} = M_{total\ S(1a)} * C_{carbon\ (1a)}$	• The conversion efficiency in the furnace is 96% (based on discussions with plant personnel). • $C_{So(1)} = 99.5$ % (plant information)
1b		• $M_{lime\ (CaOH)2\ (1a)} = 0.17$ (design specs) • $M_{Filter\ aid\ (1a)} = 0.35$ (design specs) • $M_{Activated\ clay\ (1a)} = 2$ (design specs)
2	$M_{So\ (2)} = M_{total(S2)} * C_{So(1a)}$ $M_{ash(2)} = M_{total\ (S2)} * C_{ash(1a)}$ $M_{carbon\ (2)} = M_{total\ (S2)} * C_{carbon(1a)}$ $M_{lime\ (2)} = M_{total\ (S2)} * C_{lime(1b)}$ $M_{filter\ aid\ (2)} = M_{total\ (S2)} * C_{filter\ aid\ (1b)}$ $M_{activated\ clay(2)} = M_{total\ (S2)} * C_{activated\ clay(1b)}$ $M_{CaSO4(2)} = M_{total\ (S2)} * C_{CaSO4\ (2)}$	• $C_{So(1)} = 60$ % (design specs) • $M_{total(S2)} = 1.86$ (production data)
3	$M_{So(3)} = M_{So(1a)} - M_{So(2)}$	
4	$M_{So(4)} = (0.1 * M_{So(1))}$	10% excess sulphur added to furnace (based on discussion with plant personnel).
5	$M_{methane(5)} = 0.98 * M_{natural\ gas(5)}$	• $M_{natural\ gas(5)} = 219.54$ (Methane is 98% in natural gas from production data)
6	$M_{methane(6)} = 0.98 * M_{fuel\ gas(6)}$	• $M_{fuel\ gas(6)} = 140.97$ (Methane is 98% in fuel gas from production data)
7		$M_{SO2(7)} = 40.5$ (production sheet) $M_{CO2(7)} = 362.36$ (production sheet)

8	$M_{CS2(8)} = M_{hazardous\ waste(8)} * C_{CS2(10)}$ $M_{So(8)} = M_{hazardous\ waste(8)} * C_{So(10)}$ $M_{H2S(8)} = M_{hazardous\ waste(8)} * C_{H2S(10)}$ $M_{residue(8)} = M_{hazardous\ waste(8)} * C_{residue(10)}$	• The hazardous waste stream comprises largely CS_2 with the same chemical composition as the product stream • Total flow of hazardous waste is taken from the production sheet
9		• $M_{effluent\ (9)} = 0.56$ (Production sheet)
10	$M_{total\ product\ (10)} = M_{CS2(10)} / C_{CS2(10)}$ $M_{So(10)} = M_{total\ product\ (10)} * C_{So(10)}$ $M_{H2S(10)} = M_{total\ product\ (10)} * C_{H2S(10)}$ $M_{residue(10)} = M_{total\ product\ (10)} * C_{residue(10)}$	$M_{CS2(9)} = 1000$ (unit flow)
	Where: $M_{x(y)}$ = unit mass flow per tonne of CS2 of component x in stream no y Mw_x= molar mass of species x $C_{x(y)}$ = concentration (%) of component x in stream no y (see chemical compositions below) CS_2 generation: $CH_4 + 4S = 2H_2S + CS_2$ Sulphur recovery: $2H_2S + O_2 = 2S + 2H_2O$ Overall reaction: $CH_4 + 2S + O_2 = CS2 + 2H_2O$	

Table C 4: Stream Compositions (New CS_2 process)

Component (Mass %)	**Fresh Sulphur S1**	**Solid Waste S2**	**CS_2 product S11**
Elemental sulphur	99.5	59.92	1
Ashes	0.1	8.61	-
Acid	0.02	-	-
Carbon	0.15	11.44	-
Moisture	0.2	-	-
Arsenic	0.03	-	-
Lime($Ca(OH)_2$	-	-	-
Filter aid	-	2.93	-
Activated clay	-	14.65	-
CaSO4	-	2.44	-
CS2	-	-	98
H2S	-	-	0.4
Other (residue)	-	-	0.6

APPENDIX D: Xanthate process

Table D 1: Input and output process data for xanthate liquid (SEX). Data is expressed as per tonne of xanthate produced.

Year 2011	Electricity	Water	Nitrogen
Month	**GJ**	**m^3**	**m^3**
Jan-11	0.14	0.71	11.06
Feb-11	0.20	0.69	9.17
Mar-11	0.24	0.66	7.87
Apr-11	0.29	0.63	8.80
May-11	0.24	0.61	10.40
Jun-11	0.24	0.57	9.44
Jul-11	0.26	0.53	9.01
Aug-11	0.26	0.53	10.13
Sep-11	0.24	0.61	8.57
Oct-11	0.24	0.70	7.60
Nov-11	0.26	0.75	7.07
Dec-11	0.23	0.59	6.95
Total	2.83	7.58	106.07
Average	0.24	0.63	8.84
Per tonne of xanthate prod (100%)	0.00014	1086.74	0.01

Stoichiometric chemical equations:

Liquid xanthate (SEX): $CH_3CH_2OH + CS_2 + NaOH = CH_3CH_2OCS_2Na + H_2O$

Calculations: $M_{Xanthate} = M_{product} * C_{Xanthate}$

$$M_{CS2} = M_{Xanthate} * Mw_{CS2}/Mw_{xanthate}$$

$$M_{Alcohol} = M_{Xanthate} * Mw_{alcohol}/Mw_{xanthate}$$

$$M_{Caustic} = M_{Xanthate} * Mw_{caustic}/Mw_{xanthate}$$

Where:

- M_X = Annual production mass of X
- Cxanthate = concentration (mass %100) of xanthate in the product = 0.4 for the liquid xanthate
- Mw_X = molecular weight of X

APPENDIX E: Description of data sets used

Table E 1: Description of data sets used for the old and new CS_2 process, and xanthate process

Note : Datasets taken from ecoinvent were not modified

Materials	Selected datasets	Description of data sets (Included processes)
Electricity	Electricity from coal ZA U	Electricity production in SA using coal, the transmission network and direct emissions to air, Electricity losses during medium –voltage transmission from high-voltage are accounted for.
Steam	Heat, at hard coal industrial furnace 1-10MW/RER U	Industrial heat production. The module describes the combustion process and includes softened water requirement, coal transport, ash disposal and electricity requirement.
Nitrogen	Nitrogen, liquid, at plant/RER U	Electricity for process, cooling water and waste heat. Infrastructure for air separation plant.
Natural gas	Natural gas, at production onshore/RU U	Exploration and production of gas onshore. Data doesn't include combusted fuels for turbines, motors etc. It includes well testing (fuel requirements and emissions).
Charcoal	Charcoal, at plant/GLO U	Production of charcoal from forest wood including emissions. Infrastructure can be considered of minor importance and is neglected.
Sulphur	Secondary sulphur, at refinery/RER U	All processes on the refinery site excluding the emissions from combustion facilities, including waste water treatment, process emissions and direct discharges to rivers.
Effluent	Treatment, condensate from light oil boiler, to wastewater treatment, class 2/CH U	Infrastructure materials for municipal wastewater treatment plant, transports, dismantling. Land use burdens.
Solid waste	Disposal, municipal solid waste, 22.9% water, to sanitary landfill/CH U	Waste-specific air and water emissions from incineration, auxiliary material consumption for flue gas cleaning. Short-term emissions to river water and long-term emissions to ground water from slag compartment (from bottom slag) and residual material landfill (from solidified fly ashes and scrubber sludge). Process energy demands for MSWI.

Hazardous waste	Disposal, hazardous waste, 25% water, to hazardous waste incineration/CH U	Waste-specific air and water emissions from incineration, auxiliary material consumption for flue gas cleaning. Short-term emissions to river water and long-term emissions to ground water from residual material landfill (from solidified fly ashes and scrubber sludge). Process energy demands for HWI.
Transport (Lorry >16 tonnes)	Transport, lorry >16t, fleet average/RER U	Operation of vehicle; production, maintenance and disposal of vehicles; construction and maintenance and disposal of road.
Transport (Pipeline)	Transport, natural gas, pipeline, long distance/RER U	This dataset describes the energy consumption and the emissions linked to the transport of 1 tkm average natural gas in Europe.
Activation clay	Packing, clay products/CH U	Includes the process of packing, transportation within the plant and loading of the bags on pallets. The machines used therefore are included in the infrastructure. The waste treatment after use by the end-user and transports of the packing materials are included.
Lime	Lime, hydrated, packed, at plant/CH U	Includes the packing and one part of the total heating energy for 'production' and 'administration'
Sodium hydroxide	Sodium hydroxide, 50% in H2O, production mix, at plant/RER U	Process establishing an average European sodium hydroxide production from the three different electrolysis cell technologies (mercury, diaphragm, membrane). Module that establishes only an average of the different technologies used for sodium hydroxide production - thus no process-specific emissions are included into this dataset.
Ethyl alcohol	Ethanol from ethylene, at plant/RER U	Direct hydration of ethylene including materials, energy uses, infrastructure and emissions.
Carbon disulphide	Carbon disulphide new process, at plant/ZA U	Developed in chapter 4 of thesis. Production of carbon disulphide via methane and charcoal as raw materials in South Africa. Data includes materials, transportation of raw material and energy uses, as well as emissions.
Xanthate	liquid xanthate (SEX), new CS_2 process, at plant/ ZA U	Developed in Chapter 4 of thesis. Production of xanthate in South Africa including materials and energy use.

APPENDIX F: Process contribution of old and new carbon disulphide, and xanthate process

Table F 1: Process contribution of old and new CS_2 process

	Climate change		Human toxicity		Terrestrial acidification		Freshwater ecotoxicity		Fossil depletion	
	kg CO2 eq		kg 1,4-DB eq		kg SO2 eq		kg 1,4-DB eq		kg oil eq	
	Old CS2	**New CS2**	**Old CS2**	**New CS2**	**Old CS2**	**New CS2**	**Old CS2**	**New CS2**	**Old CS2**	**New CS2**
Process										
Steam production	1.67E+03	8.57E+02	4.92E+02	2.53E+02	1.08E+01	5.54E+00	8.80E+00	4.52E+00	3.81E+02	1.96E+02
Electricity production	1.59E+03	2.29E+02	2.62E+01	3.77E+00	1.58E+01	2.27E+00	3.45E+00	4.97E-01	4.88E+02	7.02E+01
Carbon disulphide production	1.08E+02	3.62E+02	0.00E+00	0.00E+00	3.38E+01	4.05E+01	0.00E+00	0.00E+00	0.00E+00	0.00E+00
Sulphur at refinery	2.83E+02	2.77E+02	2.98E+01	2.92E+01	2.88E+01	2.83E+01	5.06E-01	4.97E-01	1.01E+02	9.96E+01
Charcoal production	2.32E+02	-	1.07E+01	-	2.87E-01	-	1.21E-01	-	1.07E+01	-
Natural gas production	1.40E+02	1.10E+02	1.99E+00	6.37E+00	9.99E-02	1.02E+00	3.67E-02	8.05E-02	5.78E+01	5.62E+02
Nitrogen production	2.55E+01	6.61E+00	1.65E+01	4.29E+00	1.06E-01	2.75E-02	3.55E-01	9.23E-02	7.37E+00	1.91E+00
Disposal of solid waste	1.24E+01	9.27E-01	8.38E+00	8.25E-01	8.52E-03	2.22E-04	3.86E-01	4.07E-02	2.07E-01	1.40E-02
Disposal of hazardous waste	2.05E+01	5.82E+00	2.72E+00	7.72E-01	2.26E-02	6.41E-03	1.18E-01	3.34E-02	2.37E+00	6.74E-01
Wastewater treatment	1.18E-01	1.95E-01	5.05E-02	8.31E-02	2.38E-04	3.92E-04	5.72E-02	9.42E-02	1.92E-02	3.16E-02
Transport (pipeline/truck)	1.49E+01	1.94E+01	1.89E+00	5.12E-01	8.54E-02	4.04E-02	4.07E-02	1.19E-02	5.63E+00	7.42E+00
Clay production	-	1.11E-02	-	1.19E-02	-	4.83E-05	-	2.59E-04	-	3.59E-03
Lime production	-	1.29E-01	-	2.70E-03	-	1.13E-04	-	5.98E-05	-	1.59E-02
Total of all processes	**4.10E+03**	**1.87E+03**	**5.91E+02**	**2.99E+02**	**8.98E+01**	**7.77E+01**	**1.39E+01**	**5.87E+00**	**1.05E+03**	**9.37E+02**
Relative performance (%)	**100**	**46**	**100**	**51**	**100**	**87**	**100**	**42**	**100**	**89**

Table F 2: Process Contribution of xanthate process

	Climate change (kg CO_2 eq)	**Human toxicity** (kg 1,4-DB eq)	**Terrestrial acidification** (kg SO_2 eq)	**Freshwater ecotoxicity** (kg 1,4-DB eq)	**Fossil depletion** (kg oil eq)
Process					
Carbon disulphide	1.87E+03	2.99E+02	7.76E+01	5.86E+00	9.36E+02
Sodium hydroxide	5.81E+02	5.90E+02	2.50E+00	8.73E+00	1.67E+02
Ethyl alcohol	7.60E+02	7.75E+01	1.99E+00	1.43E+00	6.68E+02
Electricity production	3.16E+02	5.19E+00	3.13E+00	6.83E-01	9.66E+01
Nitrogen production	2.14E+01	1.39E+01	8.91E-02	2.99E-01	6.19E+00
Total of all processes	**3.54E+03**	**9.85E+02**	**8.53E+01**	**1.70E+01**	**1.87E+03**

APPENDIX G: Desulphurisation flotation treatment process

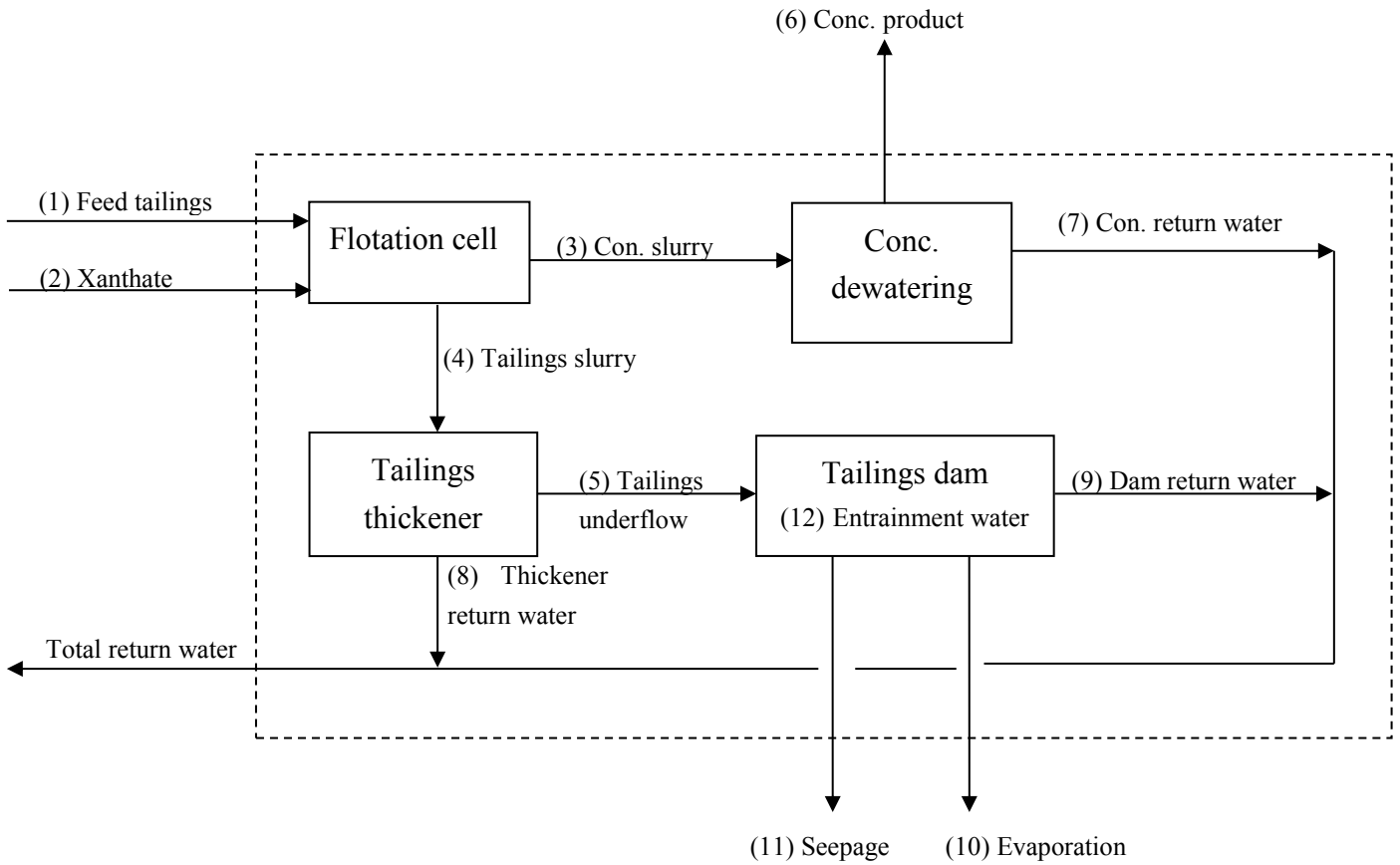


Figure G 1: Simplified Flow sheet (desulphurisation flotation treatment scenario)

Table G 1: Key mass flow parameters per management of 100 tonnes of solids tailings (Desulphurisation flotation)

	Desulphurisation flotation				**Dewatering**		**Return water**			**Dissipated water streams**		
Description	Feed tailings	Flotation reagents	Desulphur conc.	Desulphur tailings	Thickener underflow	Dewater conc.	Conc. Return H_2O	Thickener return H_2O	Dam return H_2O	Evap. H_2O	Seepage	Entrainment H_2O
Stream number	1	2	3	4	5	6	7	8	9	10	11	12
Units	tonnes/day	tonnes/day	tonnes/day	tonnes/day	tonnes/day	tonnes/day	tonnes/day	tonnes/day	tonnes/day	tonnes/day	tonnes/day	tonnes/day
Solids	100		28	72	72	28						
Water	233.3		34.22	199.11	48.00	3.11	31.11	151.11	12	19.20	2.40	14.4
Slurry	333.3		62.2	271.11	120.00	31.11						
Sulphides minerals, solids												
Total sulphur	10		9.1	0.90	0.90	9.10						
S (sulphide)	9.38		8.54	0.84	0.84	8.54						
S (sulphate)	0.62		0.56	0.06	0.06	0.56						
Zn	0.13		0.12	0.01	0.013	0.12						
Cu	0.03		0.02	0.01	0.012	0.02						
Fe	8.13		7.38	0.75	0.75	7.38						
Pyrite (FeS_2)	17.4		15.83	1.57	1.57	15.83						
Sphalerite (ZnS)	0.19		0.17	0.02	0.02	0.17						
Chalcopyrite ($CuFeS_2$)	0.10		0.05	0.05	0.05	0.05						
Xanthate	-		-	-	-	-	-	-	-	-	-	-
Calcite	2.7		0.27	2.43	2.43	0.27						
Other (gangue material)	79.61		11.67	67.94	67.94	11.67						
Total solids	100		28	72	72	28						
Soluble species		ppm										
Xanthate	0.00035	1.5	0.00014	0.0008	0.000192	0.0000125	0.000125	0.00061	0.00005	0.0000	0.000021	0.00012
Acid (H+)	-										0.00059	0.00356
S (sulphate)	-										0.0965	0.5789
Calcium	-										0.08348	0.5009
Copper	-										0.00008	0.0005
Zinc	-										0.00111	0.0067
Iron	-										0.0045	0.0270
Xanthate decomposition products												
CS2					1.02E-04						-	
Alcohol					6.15E-05				0.00005		1.91E-06	1.15E-05
Sodium hydroxide					5.34E-05				0.00005		7.53E-07	4.52E-06
Xanthic acid					1.63E-04						-	

Table G 2: Mass flows in streams (Desulphurisation flotation)

Stream No	Calculations	Assumptions and information
1	$M_{slurry(1)} = M_{solids(1)} * 30\%$ $M_{water(1)} = M_{slurry(1)} - M_{solids(1)}$ $M_{total\ sulphur(1)} = C_{total\ sulphur(1)} * M_{solids(1)}$ $M_{sulphide(1)} = C_{sulphide(1)} * M_{solids(1)}$ $M_{sulphate(1)} = C_{sulphate(1)} * M_{solids(1)}$ $M_{Zn(1)} = C_{Zn(1)} * M_{solids(1)}$ $M_{Cu(1)} = C_{Cu(1)} * M_{solids(1)}$ $M_{Fe(1)} = C_{Fe(1)} * M_{solids(1)}$ $M_{pyrite(1)} = C_{pyrite(1)} * M_{solids(1)}$ $M_{sphalerite(1)} = C_{sphalerite(1)} * M_{solids(1)}$ $M_{chalcopyrite(1)} = C_{chalcopyrite(1)} * M_{solids(1)}$ $M_{calcite(1)} = C_{calcite(1)} * M_{solids(1)}$ $C_{other(1)} = 100-(M_{pyrite(1)} + M_{sphalerite(1)} + M_{chalcopyrite(1)} + M_{calcite(1)})$ $M_{other(1)} = C_{other} *(100/M_{solids(1)})$ $M_{xanthate(1)} = 1.5 / 10\text{^}6 * M_{water(1)}$	$M_{solids(1)} = 100$ (unit flow) • Feed tailings are 30% solids • Xanthate residue in tailings feed slurry is 1.5ppm • Concentration of elements (Cu, Fe and Zn) is calculated from the weight percentage of minerals as given in literature: Pyrite (FeS_2) = 17.4% Sphalerite (ZnS) = 0.19% Chalcopyrite ($CuFeS_2$) = 0.1% Where: $C_{Cu} = C_{CuFeS2}*(Mw_{Cu}/ Mw_{CuFeS2})$ $C_{Fe} = C_{FeS2}*(Mw_{Fe}/ Mw_{FeS2}) + C_{CuFeS2}* (Mw_{Fe}/ Mw_{CuFeS2})$ $C_{Zn} = C_{ZnS}*(Mw_{Zn}/ Mw_{ZnS})$
2	$M_{xanthate,\ solid(2)} = M_{solids(1)} * 90 / 10\text{^}6$	• Xanthate addition is 90g/tonne of tailings
3	$M_{solids(3)} = M_{solids(1)} * 28\%$ $M_{slurry(3)} = M_{solids(3)} * 100\% /45\%$ $M_{water(3)} = M_{slurry(3)} - M_{solids(3)}$ $M_{total\ sulphur(3)} = M_{sulphur(1)} * 91\%$ $M_{sulphide(3)} = M_{sulphide(1)} * 91\%$ $M_{sulphate(3)} = M_{sulphide(3)} - M_{sulphide(3)}$ $M_{Zn(3)} = M_{Zn(1)} * 90\%$ $M_{Cu(3)} = M_{Cu(1)} * 60.5\%$	• 28% of the concentrate reports to the tailings • The solids content of the concentrate is 45 % • Recovery of total and sulphide sulphur to the concentrate is 91% • Recovery of Zn to the concentrate is 90% • Recovery of Cu to the concentrate is 60.5%

	$M_{Fe(3)} = (M_{chalcopyrite(3)} * Mw_{Fe} / Mw_{chalcopyrite}) + (M_{pyrite(3)} * Mw_{Fe} / Mw_{pyrite})$ $M_{pyrite(3)} = (M_{sulphide(3)} - (M_{sphalerite(3)} * Mw_S / Mw_{sphalerite}) - (M_{chalcopyrite(3)} * 2 * Mw_S / Mw_{chalcopyrite})) * Mw_{pyrite} / (2 * Mw_S)$ $M_{sphalerite(3)} = M_{Zn(3)} * Mw_{sphalerite} / Mw_{Zn}$ $M_{chalcopyrite(3)} = M_{Cu(3)} * Mw_{chalcopyrite} / Mw_{Cu}$ $M_{xanthate(3)} = M_{xanthate(2)} * 90\%$ $M_{calcite(3)} = M_{calcite(1)} * 10\%$ $M_{other(3)} = M_{solids(3)} - (M_{pyrite\ (3)} + M_{sphalerite(3)} + M_{chalcopyrite(3)} + M_{xanthate(3)} + M_{calcite(3)})$ $M_{xanthate,\ soluble\ species(3)} = (10\% * (M_{xanthate(1)} + M_{xanthate(2)}) * (M_{water(3)} / (M_{water(3)} + M_{water(4)}))$	• 90% of the added xanthate is adsorbed to the solid concentrate phase • 10% of the calcite deports to the concentrate • 10% of the xanthate deports to the solution during flotation, giving rise to a soluble xanthate concentration in the flotation cell of 4 ppm.
4	$M_{solids(4)} = M_{solids(1)} - M_{solids(3)}$ $M_{water(4)} = M_{water(1)} - M_{water(3)}$ $M_{slurry(4)} = M_{slurry(1)} - M_{slurry(3)}$ $M_{total\ sulphur(4)} = M_{total\ sulphur(1)} - M_{total\ sulphur(3)}$ $M_{sulphide(4)} = M_{sulphide(1)} - M_{sulphide(3)}$ $M_{sulphate(4)} = M_{sulphate(1)} - M_{sulphate(3)}$ $M_{Zn(4)} = M_{Zn(1)} - M_{Zn(3)}$ $M_{Cu(4)} = M_{Cu(1)} - M_{Cu(3)}$ $M_{Fe(4)} = M_{Fe(1)} - M_{Fe(3)}$ $M_{pyrite(4)} = M_{pyrite(1)} - M_{pyrite(3)}$ $M_{sphalerite(4)} = M_{sphalerite(1)} - M_{sphalerite(3)}$ $M_{chalcopyrite(4)} = M_{chalcopyrite(1)} - M_{chalcopyrite(3)}$ $M_{calcite(4)} = M_{calcite(1)} - M_{calcite(3)}$ $M_{other(4)} = M_{other(1)} - M_{other(3)}$ $M_{xanthate,\ soluble\ species(4)} = (M_{xanthate,\ soluble\ species(2)} * 10\%) * (M_{water(4)} / (M_{water(4)} + M_{water(3)}))$	
5	$M_{solids(5)} = M_{solids(4)}$	• Underflow solids content is 60%

	$M_{water(5)} = M_{slurry(5)} - M_{solids(5)}$ $M_{slurry(5)} = M_{solids(5)} * 100\% / 70\%$ $M_{total\ sulphur(5)} = M_{total\ sulphur(4)}$ $M_{sulphide(5)} = M_{sulphide(4)}$ $M_{sulphate(5)} = M_{sulphate(4)}$ $M_{Zn(5)} = M_{Zn(4)}$ $M_{Cu(5)} = M_{Cu(4)}$ $M_{Fe(5)} = M_{Fe(4)}$ $M_{pyrite(5)} = M_{pyrite(4)}$ $M_{sphalerite(5)} = M_{sphalerite(4)}$ $M_{chalcopyrite(5)} = M_{chalcopyrite(4)}$ $M_{calcite(5)} = M_{calcite(4)}$ $M_{other(5)} = M_{other(4)}$ $M_{xanthate,\ soluble\ species(5)} = (M_{xanthate,\ soluble\ species(4)} * 10\text{^}6 / M_{water(4)}) * (M_{water(5)} / 10\text{^}6)$ $M_{carbon\ disulphide,\ xanthate\ decomposition\ products(5)} = (M_{xanthate,\ soluble\ species(5)} / M_{Wxanthate} * M_{Wcarbon\ disulphide}$ $M_{alcohol,\ xanthate\ decomposition\ products(5)} = (M_{xanthate,\ soluble\ species(5)} / M_{Wxanthate} * M_{Walcohol}$ $M_{sodiun\ hydroxide,\ xanthate\ decomposition\ products(5)} = (M_{xanthate,\ soluble\ species(5)} / M_{Wxanthate} * M_{Wsodium\ hydroxide}$ $M_{xanthic\ acid,\ xanthate\ decomposition\ products(5)} = (M_{xanthate,\ soluble\ species(5)} / M_{Wxanthate} * M_{Wxanthic\ acid}$	• The solids content of the dewatered concentrate is 90% • No chemical changes occur during thickening.
6	$M_{solids(6)} = M_{solids(3)}$ $M_{water(6)} = M_{slurry(6)} - M_{solids(6)}$ $M_{total\ sulphur(6)} = M_{total\ sulphur(3)}$ $M_{sulphide(6)} = M_{sulphide(3)}$ $M_{sulphate(6)} = M_{sulphate(3)}$ $M_{Zn(6)} = M_{Zn(3)}$ $M_{Cu(6)} = M_{Cu(3)}$ $M_{Fe(6)} = M_{Fe(3)}$	• Solids content in dewatered concentrate product is 90%

	$M_{pyrite(6)} = M_{pyrite(3)}$ $M_{sphalerite(6)} = M_{sphalerite(3)}$ $M_{chalcopyrite(6)} = M_{chalcopyrite(3)}$ $M_{calcite(6)} = M_{calcite(3)}$ $M_{other(6)} = M_{other(3)}$ $M_{xanthate,\ soluble\ species(6)} = (M_{xanthate,\ soluble\ species(4)} * 10\text{^}6 / M_{water(4)}) * (M_{water(6)} / 10\text{^}6)$	
7	$M_{water(7)} = M_{water(3)} - M_{water(6)}$ $M_{xanthate,\ soluble\ species(7)} = (M_{xanthate,\ soluble\ species(3)} - M_{xanthate,\ soluble\ species(6)}$	
8	$M_{water(8)} = M_{water(4)} - M_{water(5)}$ $M_{xanthate,\ soluble\ species(8)} = (M_{xanthate,\ soluble\ species(4)} * 10\text{^}6 / M_{water(4)}) * (M_{water(8)} / 10\text{^}6)$	
9	$M_{water(9)} = M_{water(5)} * 25\%$ $M_{xanthate,\ soluble\ species(9)} = (M_{xanthate,\ soluble\ species(4)} * 10\text{^}6 / M_{water(4)}) * (M_{water(9)} / 10\text{^}6)$ $M_{alcohol,\ xanthate\ decomposition\ product\ (9)} = (M_{xanthate,\ soluble\ species(4)} * 10\text{^}6 / M_{water(4)}) * (M_{water(9)} / 10\text{^}6)$ $M_{sodium\ hydroxide,\ xanthate\ decomposition\ product\ (9)} = (M_{xanthate,\ soluble\ species(4)} * 10\text{^}6 / M_{water(4)}) * (M_{water(9)} / 10\text{^}6)$	• Return water is 25% of tailings thickener underflow
10	$M_{water(10)} = M_{water(5)} * 40\%$	• Evaporated water is 40% of tailings thickener underflow
11	$M_{water(11)} = M_{water(5)} * 5\%$ $M_{xanthate,\ soluble\ species(11)} = (M_{xanthate,\ soluble\ species(5)} - M_{xanthate,\ soluble\ species(9)}) * M_{water(11)} / (M_{water(11)} + M_{water(12)})$ $M_{alcohol,\ xanthate\ decomposition\ product\ (11)} = (M_{alcohol,\ xanthate,\ decomposition\ product\ (5)} - M_{alcohol,\ xanthate\ decomposition\ product\ (9)}) * M_{water\ (11)} / (M_{water\ (11)} + M_{water\ (12)})$ $M_{sodium\ hydroxide,\ xanthate\ decomposition\ product\ (11)} = (M_{sodium\ hydroxide,\ xanthate,\ decomposition\ product\ (5)} - M_{sodium\ hydroxide,\ xanthate\ decomposition\ product\ (9)}) * M_{water(11)} / (M_{water(11)} + M_{water(12)})$	• Seepage from tailings storage facility is 5% of tailings thickener underflow • MPA/ AP: Conversion sulphide (%) to acid (kg H2SO4/t of solids) is 30.625 • NP (kg H2SO4/ tonne of solids) = 9.8 * % CaCO3 • Oxidation of sulphide S in tailings pore water is 100% and results in stoichiometric formation of sulphuric acid • Neutralisation of acid formed through of sulphuric acid occurs through calcite dissolution.

	Acid production MPA/AP: $M_{H2SO4(AP)} = (M_{sulphide(4)} * 100 / M_{solids(4)}) * 30.625 * 2 / Mw_{H2SO4}$ ANC/NP: $M_{H2SO4(NP)} = (M_{calcite(4)} * 100 / M_{solids(4)}) * 9.8 * 2 / Mw_{H2SO4}$ $M_{acid(11)} = ((M_{H2SO4(AP)} - M_{H2SO4(NP)}) * M_{solids(5)}) * (M_{water(11)} / (M_{water(11)} + M_{water(12)}))$ $M_{sulphate(11)} = (M_{sulphide(4)} * 80\%) * (M_{water(11)} / (M_{water(11)} + M_{water(12)}))$ $M_{calcium(11)} = (M_{calcite(5)} * Mw_{ca} * 60\%) * (M_{water(11)} / (M_{water(11)} + M_{water(12)}))$ $M_{Cu11)} = (M_{Cu(5)} * 5\%) * (M_{water(11)} / (M_{water(11)} + M_{water(12)}))$ $M_{Zn(11)} = (M_{Zn(5)} * 60\%) * (M_{water(11)} / (M_{water(11)} + M_{water(12)}))$ $M_{iron(11)} = (M_{pyrite(5)} * 2\%) * (M_{water(11)} / (M_{water(11)} + M_{water(12)}))$	• Net mobilisation of sulphate in tailings pore water is 80% • Net mobilisation of Ca in tailings pore water is 60% • Net mobilisation of Cu in tailings pore water is 5% • Net mobilisation of Zn in tailings pore water is 60% • Net mobilisation of iron in tailings pore water is 2%
12	$M_{water(12)} = M_{water(5)} * 30\%$ $M_{xanthate, soluble species(12)} = (M_{xanthate, soluble species(5)} - M_{xanthate, soluble species(9)}) * M_{water(12)} / (M_{water(11)} + M_{water(12)})$ $M_{alcohol, xanthate decomposition product (12)} = (M_{alcohol, xanthate decomposition product (5)} - M_{alcohol, xanthate decomposition product (9)}) * M_{water(12)} / (M_{water(11)} + M_{water(12)})$ $M_{sodium hydroxide, xanthate decomposition product (12)} = (M_{sodium hydroxide, xanthate decomposition product (5)} - M_{sodium hydroxide, xanthate decomposition product (9)}) * M_{water(12)} / (M_{water(11)} + M_{water(12)})$ $M_{acid(12)} = ((M_{H2SO4(AP)} - M_{H2SO4(NP)}) * M_{solids(5)}) * (M_{water(12)} / (M_{water(11)} + M_{water(12)}))$ $M_{sulphate(12)} = (M_{sulphide(4)} * 80\%) - M_{sulphate(11)}$ $M_{calcium(12)} = (M_{calcite(5)} * Mw_{ca} * 60\%) - M_{calcium(11)}$ $M_{Cu(12)} = (M_{Cu(5)} * 5\%) - M_{Cu(11)}$ $M_{Zn(12)} = (M_{Zn(5)} * 60\%) - M_{Zn(11)}$ $M_{iron(12)} = (M_{pyrite(5)} * 2\%) - M_{iron(11)}$	• Entrainment of water in the tailings storage facility is 30% of tailings thickener underflow

	Where: $M_{x(y)}$ = unit mass flow per tonne of solid tailings of component x in stream no y Mw_x= molar mass of species x $C_{x(y)}$ = concentration (%) of component x in stream no y (see chemical compositions below) **Reactions:** $FeS_2 + 3O_2 + 2H_2O = Fe^{2+} + 2H_2SO_4$ $CuFeS_2 + 3O_2 + 2H_2O = CuFe + 2H_2SO_4$ $ZnS + 3O_2 + 2H_2O = 2Zn + 2H_2SO_4$ $H_2SO_4 + CaCO_3 = CaSO_4 + H_2O + CO_2$ **Decomposition of xanthate:** $C_2H_5OCS_2Na + H_2O \rightarrow C_2H_5OCS_2H + NaOH$ $C_2H_5OCS_2H \rightarrow CS_2 + C_2H_5OH$

Table G 3: Stream composition (Desulphurisation flotation)

Component (Mass %)	Feed tailings S1
Total sulphur	10
S (sulphide)	9.38
S (sulphate)	0.62
Zn	0.13
Cu	0.03
Fe	8.13
Pyrite	17.4
Sphalerite	0.19
Chalcopyrite	0.1
Calcite	2.70
Other (gangue material)	79.61

APPENDIX H: Conventional treatment process (Base case)

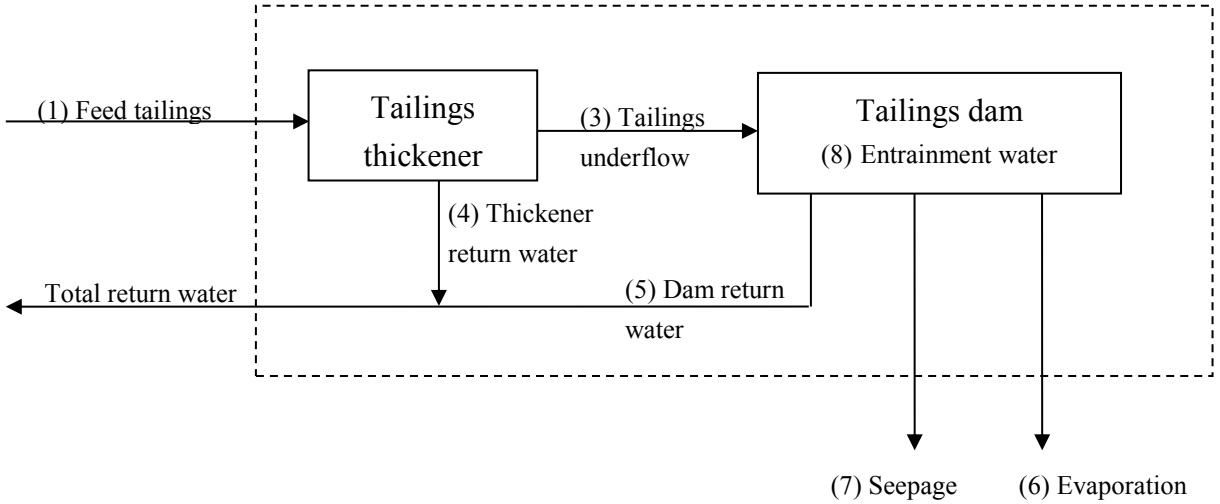


Figure H 1: Simplified Flow sheet (Base case)

Table H 1: Key mass flow parameters per management of 100 tonnes of tailings (Base case)

Description	Feed tailings	Thickener underflow	Thickener return H_2O	Dam return H_2O	Evap. H_2O	Seepage	Entrainment H_2O
Stream number	**1**	**3**	**4**	**5**	**6**	**7**	**8**
Units	**tonnes/day**	**tonnes/day**	**tonnes/day**	**tonnes/day**	**tonnes/day**	**tonnes/day**	**tonnes/day**
Solids	100	100					
Water	233.3	66.67	166.67	16.67	26.67	3.33	20.00
Slurry	333.3	166.7					
Sulphides minerals, solids							
Total sulphur	10	10					
S (sulphide)	9.38	9.38					
S (sulphate)	0.62	0.62					
Zn (zinc)	0.13	0.13					
Cu (copper)	0.03	0.03					
Fe (iron)	8.13	8.13					
Pyrite (FeS_2)	17.4	17.4					
Sphalerite (ZnS)	0.19	0.19					
Chalcopyrite ($CuFeS_2$)	0.10	0.10					
Xanthate	-	-	-	-	-	-	-
Calcite	2.7	2.7					
Other (gangue material)	79.61	79.61					
Total solids	100	100					
Soluble species							
Xanthate	0.00035	0.0001	0.000250	0.000025	0	0.000011	0.000041
Acid (H+)	-					0.07597	0.45585
S (sulphate)	-					1.07200	6.43200
Calcium	-					0.09257	0.55543
Copper	-					0.00021	0.00129
Zinc	-					0.01093	0.06686
Iron	-					0.04971	0.29829
Xanthate decomposition products							
CS2		5.28E-05					
Alcohol		3.19E-05		0.000025		9.93E-07	5.96E-06
Sodium hydroxide		2.77E-05		0.000025		3.91E-07	2.35E-06
Xanthic acid		8.48E-05					

Table H 2: Mass flows in streams (Base case)

Stream No	Calculations	Assumptions and information
1	$M_{slurry(1)} = M_{solids(1)} * 30\%$ $M_{water(1)} = M_{slurry(1)} - M_{solids(1)}$ $M_{total\ sulphur(1)} = C_{total\ sulphur(1)} * M_{solids(1)}$ $M_{sulphide(1)} = C_{sulphide(1)} * M_{solids(1)}$ $M_{sulphate(1)} = C_{sulphate(1)} * M_{solids(1)}$ $M_{Zn(1)} = C_{Zn(1)} * M_{solids(1)}$ $M_{Cu(1)} = C_{Cu(1)} * M_{solids(1)}$ $M_{Fe(1)} = C_{Fe(1)} * M_{solids(1)}$ $M_{pyrite(1)} = C_{pyrite(1)} * M_{solids(1)}$ $M_{sphalerite(1)} = C_{sphalerite(1)} * M_{solids(1)}$ $M_{chalcopyrite(1)} = C_{chalcopyrite(1)} * M_{solids(1)}$ $M_{calcite(1)} = C_{calcite(1)} * M_{solids(1)}$ $M_{other(1)} = C_{other(1)} * M_{solids(1)}$ $M_{xanthate(1)} = 1.5 / 10\text{^}6 * M_{water(1)}$	$M_{solids(1)} = 100$ (unit flow) • Feed tailings are 30% solids • Xanthate residue in tailings feed slurry is 1.5ppm
3	$M_{solids(3)} = M_{solids(1)}$ $M_{water(3)} = M_{slurry(3)} - M_{solids(3)}$ $M_{slurry(3)} = M_{solids(3)} * 100\% / 70\%$ $M_{total\ sulphur(3)} = M_{total\ sulphur(1)}$ $M_{sulphide(3)} = M_{sulphide(1)}$ $M_{sulphate(3)} = M_{sulphate(1)}$ $M_{Zn(3)} = M_{Zn(1)}$ $M_{Cu(3)} = M_{Cu(1)}$ $M_{Fe(3)} = M_{Fe(1)}$ $M_{pyrite(3)} = M_{pyrite(1)}$	• Underflow solids is 70%

	$M_{sphalerite(3)} = M_{sphalerite(1)}$ $M_{chalcopyrite(3)} = M_{chalcopyrite(1)}$ $M_{calcite(3)} = M_{calcite(1)}$ $M_{other(3)} = M_{other(1)}$ $M_{xanthate, soluble species(3)} = 1.5 * M_{water(3)} / 10^6$ $M_{carbon disulphide, xanthate decomposition products(3)} = (M_{xanthate, soluble species(3)} / M_{Wxanthate} * M_{Wcarbon disulphide}$ $M_{alcohol, xanthate decomposition products(3)} = (M_{xanthate, soluble species(3)} / M_{Wxanthate} * M_{Walcohol}$ $M_{sodiun hydroxide, xanthate decomposition products(3)} = (M_{xanthate, soluble species(3)} / M_{Wxanthate} * M_{Wsodium hydroxide}$ $M_{xanthic acid, xanthate decomposition products(3)} = (M_{xanthate, soluble species(3)} / M_{Wxanthate} * M_{Wxanthic acid}$	
4	$M_{water(4)} = M_{water(1)} - M_{water(3)}$ $M_{xanthate, soluble species(4)} = 1.5 * M_{water(4)} / 10^6$	
5	$M_{water(5)} = M_{water(3)} * 25\%$ $M_{xanthate, soluble species(5)} = 1.5 * M_{water(5)} / 10^6$ $M_{alcohol, xanthate decomposition products(5)} = 1.5 * M_{water(5)} / 10^6$ $M_{sodiun hydroxide, xanthate decomposition products(5)} = 1.5 * M_{water(5)} / 10^6$	• Return water is 25% of tailings thickener underflow
6	$M_{water(6)} = M_{water(3)} * 40\%$	• Evaporated water is 40% of tailings thickener underflow
7	$M_{water(7)} = M_{water(3)} * 5\%$ $M_{xanthate, soluble species(7)} = (M_{xanthate, soluble species(3)} - M_{xanthate, soluble species(5)}) * M_{water(7)} / (M_{water(7)} + M_{water(8)})$ $M_{alcohol, xanthate decomposition product (7)} = (M_{alcohol, xanthate, decomposition product (3)} - M_{alcohol, xanthate decomposition product (5)}) * M_{water (7)} / (M_{water (8)} + M_{water (7)})$ $M_{sodium hydroxide, xanthate decomposition product (7)} = (M_{sodium hydroxide, xanthate, decomposition product (3)} - M_{sodium hydroxide, xanthate decomposition product (5)}) * M_{water(7)} / (M_{water(8)} + M_{water(7)})$ **Acid production** MPA/AP: $M_{H2SO4(AP)} = C_{sulphide(1)} * 30.625 * 2 / Mw_{H2SO4}$	• Seepage from tailings storage facility is 5% of tailings thickener underflow • Xanthate does not decompose to CS_2 • MPA/ AP: Conversion sulphide (%) to acid (kg H2SO4/t of solids) is 30.625 • NP (kg H2SO4/ tonne of solids) = 9.8 * % CaCO3 • Oxidation of sulphide S in tailings pore water is 100% • Mobilisation of sulphate in tailings

	ANC/NP: $M_{H2SO4(NP)} = C_{calcite(1)} * 9.8 * 2 / Mw_{H2SO4}$ $M_{acid(7)} = ((M_{H2SO4(AP)} - M_{H2SO4(NP)}) * M_{solids(3)}) * (M_{water(7)} / (M_{water(7)} + M_{water(8)}))$ $M_{sulphate(7)} = (M_{sulphide(3)} * 80\%) * (M_{water(7)} / (M_{water(7)} + M_{water(8)}))$ $M_{calcium(7)} = (M_{calcite(3)} * Mw_{ca} * 60\%) * (M_{water(7)} / (M_{water(7)} + M_{water(8)}))$ $M_{Cu(7)} = (M_{Cu(3)} * 5\%) * (M_{water(7)} / (M_{water(7)} + M_{water(8)}))$ $M_{Zn(7)} = (M_{Zn(3)} * 60\%) * (M_{water(7)} / (M_{water(7)} + M_{water(8)}))$ $M_{iron(7)} = (M_{pyrite(3)} * 2\%) * (M_{water(7)} / (M_{water(7)} + M_{water(8)}))$	pore water is 80% • Mobilisation of Ca in tailings pore water is 60% • Mobilisation of Cu in tailings pore water is 5% • Mobilisation of Zn in tailings pore water is 60% • Mobilisation of iron in tailings pore water is 2%
8	$M_{water(8)} = M_{water(3)} * 30\%$ $M_{xanthate, soluble species(8)} = (M_{xanthate, soluble species(3)} - M_{xanthate, soluble species(5)}) * M_{water(8)} / (M_{water(7)} + M_{water(8)})$ $M_{alcohol, xanthate decomposition product (8)} = (M_{alcohol, xanthate decomposition product (3)} - M_{alcohol, xanthate decomposition product (5)}) * M_{water(8)} / (M_{water(7)} + M_{water(8)})$ $M_{sodium hydroxide, xanthate decomposition product (8)} = (M_{sodium hydroxide, xanthate decomposition product (3)} - M_{sodium hydroxide, xanthate decomposition product (5)}) * M_{water(8)} / (M_{water(7)} + M_{water(8)})$ $M_{acid(8)} = ((M_{H2SO4(AP)} - M_{H2SO4(NP)}) * M_{solids(3)}) * (M_{water(8)} / (M_{water(7)} + M_{water(8)}))$ $M_{sulphate(8)} = (M_{sulphide(3)} * 80\%) - M_{sulphate(7)}$ $M_{calcium(8)} = (M_{calcite(3)} * Mw_{ca} * 60\%) - M_{calcium(7)}$ $M_{Cu(8)} = (M_{Cu(3)} * 5\%) - M_{Cu(7)}$ $M_{Zn(8)} = (M_{Zn(3)} * 60\%) - M_{Zn(7)}$ $M_{iron(8)} = (M_{pyrite(3)} * 2\%) - M_{iron(7)}$	• Entrainment of water in the tailings storage facility is 30%
	Where: $M_{x(y)}$ = unit mass flow per tonne of CS_2 of component x in stream no y Mw_x= molar mass of species x $C_{x(y)}$ = concentration (%) of component x in stream no y (see chemical compositions below)	

APPENDIX I: Process contribution to impact categories - USEtox and ReCiPe method

Table I 1 : Process contribution to impacts – USEtox (Scenario A)

Desulphurisation					
Impact category	**Unit**	**Total**	**Foreground process**	**Background processes**	
			Desulphurisation flotation	**Xanthate**	**Electricity**
Human toxicity	CTUh	1.49E-03	1.41E-03	3.92E-06	7.54E-05
Ecotoxicity	CTUe	4.96E+04	4.80E+04	5.10E+01	1.56E+03

Base case				
Impact category	**Unit**	**Total**	**Foreground process**	**Background processes**
			Base case	**Electricity**
Human toxicity	CTUh	1.41E-02	1.41E-02	1.87E-05
Ecotoxicity	CTUe	4.36E+05	4.36E+05	3.86E+02

Table I 2 : Process contribution to impacts – USEtox (Scenario B)

Desulphurisation					
Impact category	**Unit**	**Total**	**Foreground process**	**Background processes**	
			Desulphurisation flotation	**Xanthate**	**Electricity**
Human toxicity	CTUh	1.58E-03	1.50E-03	3.55E-06	7.50E-05
Ecotoxicity	CTUe	4.89E+09	4.89E+09	4.34E+01	1.55E+03

Base case				
Impact category	**Unit**	**Total**	**Foreground process**	**Background processes**
			Base case	**Electricity**
Human toxicity	CTUh	1.41E-02	1.41E-02	1.87E-05
Ecotoxicity	CTUe	4.36E+05	4.36E+05	3.86E+02

Table I 3 : Process contribution to impacts – ReCiPe method

Desulphurisation					
Impact category	**Unit**	**Total**	**Foreground process**	**Background processes**	
			Desulphurisation flotation	**Xanthate**	**Electricity**
Climate change	kg CO_2 eq	5.82E+02	0.00E+00	1.74E+01	5.68E+02
Human toxicity	kg 1,4-DB eq	2.21E+02	3.98E+01	5.63E+00	1.77E+02
Terrestrial acidification	kg SO_2 eq	5.11E+00	0.00E+00	4.07E-01	4.73E+00
Freshwater ecotoxicity	kg 1,4-DB eq	1.22E+01	8.27E+00	9.66E-02	3.82E+00
Urban land occupation	m^2a	8.62E+01	8.51E+01	-	1.11E+00
Natural land transformation	m^2	2.72E-01	2.62E-01	2.00E-03	7.40E-03
Fossil depletion	kg oil eq	1.13E+02	0.00E+00	8.72E+00	1.05E+02

Base case				
Impact category	**Unit**	**Total**	**Foreground process**	**Background processes**
			Base case	**Electricity**
Climate change	kg CO_2 eq	1.41E+02	0.00E+00	1.41E+02
Human toxicity	kg 1,4-DB eq	4.42E+02	3.98E+02	4.39E+01
Terrestrial acidification	kg SO_2 eq	1.17E+00	0.00E+00	1.17E+00
Freshwater ecotoxicity	kg 1,4-DB eq	8.37E+01	8.27E+01	9.50E-01
Urban land occupation	m^2a	1.18E+02	1.18E+02	2.70E-01
Natural land transformation	m^2	3.70E-01	3.60E-01	0.00E+00
Fossil depletion	kg oil eq	2.60E+01	0.00E+00	2.60E+01

APPENDIX J: Characterisation factors of contributing substances

Table J 1: Characterisation factors on human toxicity and ecotoxicity to each of the substances emitted to ground water

	ReCiPe method		USEtox method	
Substances	**Human toxicity** (kg 1,4-DB eq)	**Freshwater ecotoxicity** (kg 1,4-DB eq)	**Human toxicity** (CTUh)	**Freshwater ecotoxicity** (CTUe)
Zinc ion	36.2	7.52	1.28E-03	38600
Copper ion	-	-	8.63E-07	55200
Manganese	700	4.41	-	-
Xanthate	-	-	-	548
*Carbon disulphide	10.3	4.75E-05	4.67E-05	2.31
Alcohol	-	-	-	1670
Sodium hydroxide	-	-	-	-
Acid (H+)	-	-	-	-
Sulphur (S)	-	-	-	-
Iron (Fe)	-	-	-	-
Calcium (Ca)	-	-	-	-

- Cells marked with '–' mean that the method does not have a characterisation factor for the considered substance.
- * substance emitted to air

APPENDIX K: Sensitivity analysis

Table K 1: Sensitivity analysis for electricity consumption

Base case	Climate change		Fossil depletion		Acidification	
	(kg CO2 eq)	Percentage change (%)	(kg oil eq)	Percentage change (%)	(kg SO2 eq)	Percentage change (%)
(163000 kJ/tonne)	56.11	60.18	10.35	60.18	0.468	60.14
(Assumed value) (407500 kJ/tonne)	140.90	0.00	26.00	0.00	1.174	0
(815000 kJ/tonne)	280.55	99.12	51.76	99.11	2.338	99.15

Desulphurisation	Climate change		Fossil depletion		Acidification	
	(kg CO2 eq)	Percentage change (%)	(kg oil eq)	Percentage change (%)	kg SO2 eq	Percentage change (%)
(2282000kJ/tonne)	808.00	38.82	155.00	37.31	6.99	36.79
(1956000 kJ/tonne)	695.00	19.41	134.00	18.70	6.05	18.40
(Assumed value) (1630000 kJ/tonne)	582.05	0.00	112.89	0.00	5.11	0
(1304000 kJ/tonne)	469.00	19.42	92.10	18.41	4.17	18.40
(978000 kJ/tonne)	356	38.84	71.2	36.93	3.23	36.79

***Table K 2**: Sensitivity analysis for zinc ore mineralogy*

Base case				
Total emissions (% zinc conc.)	**Human toxicity**		**Ecotoxicity**	
	(CTUh)	Percentage change (%)	(CTUe)	Percentage change (%)
0.13% (assumed value)	1.42E-02	0.00	4.40E+05	0.00
0.09%	1.00E-02	**-30**	3.13E+05	**-29**
0.05%	5.73E-03	**-60**	1.84E+05	**-58**
0.01%	1.44E-03	**-90**	5.43E+04	**-88**

Desulphurisation				
Total emissions	**Human toxicity**		**Ecotoxicity**	
(% zinc conc.)	(CTUh)	Percentage change (%)	(CTUe)	Percentage change (%)
0.13% (assumed value)	1.50E-03	**0.00**	4.89E+04	**0.00**
0.09%	1.08E-03	**-28**	3.61E+04	**-26**
0.05%	6.55E-04	**-56**	2.34E+04	**-52**
0.01%	1.41E-04	**-91**	8670.00	**-82**

***Table K 3**: Sensitivity analysis for copper ore mineralogy*

Base case				
Total emissions	**Human toxicity**		**Ecotoxicity**	
(wt %)	(CTUh)	Percentage change (%)	(CTUe)	Percentage change (%)
0.03 wt % (assumed value)	0.10	**0.00**	3.11E+06	**0.00**
0.08 wt %	0.10	**0.00**	3.23E+06	**3.86**
0.13 wt %	0.10	**0.00**	3.35E+06	**7.72**
0.17 wt %	0.10	**0.00**	3.48E+06	**11.90**

Desulphurisation				
Total emissions	**Human toxicity**		**Ecotoxicity**	
(wt %)	(CTUh)	Percentage change (%)	(CTUe)	Percentage change (%)
0.03 wt % (assumed value)	1.37E-02	0.00	4.66E+05	0.00
0.08 wt %	1.37E-02	**0.00**	5.35E+05	**14.81**
0.13 wt %	1.37E-02	**0.00**	6.12E+05	**31.33**
0.17 wt %	1.37E-02	**0.00**	6.73E+05	**44.42**

***Table K 4**: Sensitivity analysis for zinc mobilisation*

Base case				
Total emissions	**Human toxicity**		**Ecotoxicity**	
(% net mobilisation)	CTUh	Percentage change (%)	CTUe	Percentage change (%)
60% (assumed value)	1.43E-02	0.00	4.41E+05	0.00
90%	2.10E-02	46.85	6.44E+05	46.03
30%	7.01E-03	50.98	2.22E+05	49.66

Desulphurisation				
Total emissions	**Human toxicity**		**Ecotoxicity**	
(% net mobilisation)	CTUh	Percentage change (%)	CTUe	Percentage change (%)
60% (assumed value)	0.00149	0.00	4.96E+04	0.00
90%	0.00213	42.95	6.89E+04	38.91
30%	0.000719	-51.74	2.64E+04	-46.77

Base case				
Total emissions	**Human toxicity**		**Ecotoxicity**	
(% net mobilisation)	CTUh	Percentage change (%)	CTUe	Percentage change (%)
60% (assumed value)	1.43E-02	0.00	4.41E+05	0.00
60%	1.43E-02	0.00	4.41E+05	0.00

Desulphurisation				
Total emissions	**Human toxicity**		**Ecotoxicity**	
(% net mobilisation)	CTUh	Percentage change (%)	CTUe	Percentage change (%)
60% (assumed value)	1.49E-03	0.00	4.96E+04	0.00
45%	1.10E-03	26.17	3.80E+04	23.39

***Table K 5**: Sensitivity analysis for copper mobilisation*

Base case				
Total emissions	**Human toxicity**		**Ecotoxicity**	
(% net mobilisation)	(CTUh)	Percentage change (%)	(CTUe)	Percentage change (%)
5% (assumed value)	1.43E-02	0.0	4.41E+05	0.0
10%	1.43E-02	**0.0**	4.53E+05	**3**
1%	1.43E-02	**0.0**	4.31E+05	**2.3**

Desulphurisation				
Total emissions	**Human toxicity**		**Ecotoxicity**	
(% net mobilisation)	(CTUh)	Percentage change (%)	(CTUe)	Percentage change (%)
5% (assumed value)	1.49E-03	0.0	4.96E+04	0
10%	1.49E-03	**0.0**	5.51E+04	**11**
1%	1.49E-03	**0.0**	4.52E+04	**-8.9**

***Table K 6 :** Sensitivity analysis for xanthate deportment*

Desulphurisation				
Total emissions	**Human toxicity**		**Ecotoxicity**	
(% xanthate to tailings)	(CTUh)	Percentage change (%)	(CTUe)	Percentage change (%)
10**% (assumed value)**	1.49E-03	**0.00**	4.96E+04	**0.00**
5%	1.49E-03	**0**	4.96E+04	**0**
15%	1.49E-03	**0**	4.96E+04	**0**
20%	1.49E-03	**0**	4.96E+04	**0**